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DEFECT CHEMISTRY AND CHARACTERIZATION OF $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

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(NASA-CR-161746) DEFECT CHEMISTRY AND
CHARACTERIZATION OF $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

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I. FOREWORD

This semiannual technical report covers the work performed by Honeywell Electro-Optics Center, Lexington, Massachusetts from January 1979 to June 1980 under the NASA sponsored program entitled 'Defect Chemistry and Characterization of (Hg,Cd)Te' on Contract No. NAS8-33245. The objective of this program is to study and formalize the defect chemistry of (Hg,Cd)Te and to evaluate and select characterization methods for the material.

The principal investigator is Dr. H.R. Vydyanath providing the overall technical direction for the program. Assistance with the experimental work is provided by J.C. Donovan, P. Crickard and A. Barnes. R.A. Lancaster and D.A. Nelson generously furnished all the crystals required for the program.

II. INTRODUCTION

The work performed under this program is the first ever attempt of a systematic investigation of the nature of point defects in $\text{Hg}_{1-x}\text{Cd}_x\text{Te(S)}$ alloys and the mode of incorporation of the different dopants. Prior to the initiation of this program very little information existed in literature on the systematic investigation of defects in this technologically important infrared detector material. At the end of the 18 month period of the program, significant accomplishments have been made toward understanding the nature of lattice defects and the mode of incorporation of different dopants. For the first time in literature, the defect structures of undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te(S)}$, undoped, copper doped and indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ have been established. The native acceptor defects have been found to be doubly ionized in both $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te(S)}$ and $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$. Native donor defects are found to be negligible in concentration in these alloys and the origin of p-type to n-type conversion has been shown to be due to residual foreign donors and not due to native donor defects. Thermodynamic constant for the incorporation of the native acceptor defect has been established in both $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te(S)}$ and $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$.

A detailed investigation of copper and indium doping in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ indicates that copper is incorporated only on metal lattice sites acting as a single acceptor while indium has been shown to be incorporated as $\text{In}_2\text{Te}_3\text{(S)}$ dissolved in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ with only a small fraction of indium acting as donors, occupying Hg lattice sites. The results obtained on copper doped, and indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ are consistent with results obtained in the undoped crystals. The equilibrium constants established for the intrinsic excitation process and for the incorporation of the native acceptor defects satisfactorily account for the results obtained in copper doped and indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$.

The following presentations and publications have resulted from the work performed so far:

- (1) '(Hg_{1-x}Cd_x)Te Material Studies' H.R. Vydyanath, D.A. Nelson, R.A. Lancaster and R.G. Roy in proceedings of the IRIS Detector Specialty Group meeting, Minneapolis, MN June 15-17, 1979 p. 29.
- (2) 'Defect Chemistry and Characterization of (Hg_{1-x}Cd_x)Te' H.R. Vydyanath, D.A. Nelson and R.A. Lancaster, Journal of Electrochem. Soc. 126, 371C (1979)
- (3) 'Defect Studies in Hg_{0.8}Cd_{0.2}Te' H.R. Vydyanath, presented at the conference on the "Crystal Growth and Characterization of II-VI Compounds", University of Lancaster, U.K., April 14-16, 1980.
- (4) 'Lattice Defects in Hg_{1-x}Cd_xTe Alloys' I-Defect Structure of undoped and copper doped Hg_{0.8}Cd_{0.2}Te, H.R. Vydyanath and D.A. Nelson; submitted for publication in the Journal of Electrochemical Society.
- (5) 'Lattice Defects in Hg_{1-x}Cd_xTe Alloys' II-Defect Structure of Indium Doped Hg_{0.8}Cd_{0.2}Te, H.R. Vydyanath; submitted for publication in the Journal of Electrochemical Society.
- (6) 'Lattice Defects in Hg_{1-x}Cd_xTe Alloys' III-Defect Structure of Undoped Hg_{0.6}Cd_{0.4}Te, H.R. Vydyanath, J.C. Donovan and D.A. Nelson; submitted for publication in the Journal of Electrochemical Society.

III. TECHNICAL DETAILS

Hall effect and electrical resistivity measurements were the main tools utilized in characterizing the defects in the present program. The variation in the carrier concentration and carrier mobility in the crystals-----cooled to room temperature subsequent to anneals at high temperatures under different partial pressures of Hg---was used to arrive at defect models in the undoped as well as the doped crystals. This section dealing with the work performed from January 1979 to June 1980 presents the technical details of the work in the form of three papers that have been submitted to the Journal of the Electrochemical Society for publication. The papers describe the background material, the experimental details and the analysis of the data. Defect models for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}(\text{S})$, and $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}(\text{S})$, copper and indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}(\text{S})$ have been proposed. Thermodynamic constants for the incorporation of the native acceptor defects as well as for the intrinsic excitation process have been arrived at. These constants satisfactorily explain the experimental results in the undoped as well as the doped crystals.

III.1

**Defect chemistry and characterization of undoped and copper doped
 $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$**

LATTICE DEFECTS IN $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ALLOYS†

I DEFECT STRUCTURE OF UNDOPED AND COPPER DOPED $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

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ABSTRACT - Undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals were subjected to high temperature equilibration at temperatures ranging from 400°C to 655°C in various Hg atmospheres. Hall effect and mobility measurements were carried out on the crystals quenched to room temperature subsequent to the high temperature equilibration. The variation of the hole concentration in the cooled crystals at 77 K as a function of the partial pressure of Hg at the equilibration temperatures, together with a comparison of the hole mobility in the undoped samples with that in the copper and phosphorus doped samples has yielded a defect model for the undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals, according to which, the undoped crystals are essentially intrinsic at the equilibration temperatures and the native acceptor defects are doubly ionized. Native donor defects appear to be negligible in concentration, implying that the p to n conversion in these alloys is mainly due to residual foreign donor impurities. The thermodynamic constants for the intrinsic excitation process as well as for the incorporation of the doubly ionized native acceptor defects in the undoped crystals have been arrived at.

Copper appears to be incorporated on metal lattice sites acting as a single acceptor with little compensation. Results on the heavily copper doped samples indicate that the quench from the equilibration temperatures was imperfect resulting in a large fraction of the copper precipitating as neutral copper.

From results of experiments where the cooling rate from the equilibration temperatures was intentionally varied in the undoped samples, a qualitative correlation was established between the quenching efficiency and the presence of macroscopic defects such as voids and inclusions in the samples.

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Key words - Lattice, defects, copper doping, phosphorus doping, $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, hole mobility

INTRODUCTION

The importance of the pseudo binary semiconducting $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys as a useful infrared detector material has long been recognized [1,2]. The bandgap of these alloys is variable depending on the proportions of HgTe and CdTe present in them; the variable bandgap makes these alloys suitable for infrared detector applications over a wide spectral range.

Considerable deviations from stoichiometry arise in these alloys prepared at elevated temperatures; these deviations result in electrically active point defects which in turn influence the carrier concentration and the lifetime in the material. Very little information exists on the systematic investigation of the nature of defects and the variation of the concentration of these defects in these alloys as a function of the physicochemical conditions of preparation. In fact, much confusion prevails regarding the origin of n type in these alloys [2-5].

As part of a program aimed at investigating the defect structure of the undoped $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys as well as the mode of incorporation of dopants, the present paper reports on the study of the undoped and copper doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$.

Based on the results of Hall effect and mobility measurements on the undoped and copper doped crystals quenched to room temperature subsequent to high temperature equilibration, defect models for the undoped and copper doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ have been arrived at. Thermodynamic constants for the intrinsic excitation constant and the incorporation of the native acceptor defects have been evaluated. These constants satisfactorily explain the electrical data in the undoped as well as the copper doped crystals.

EXPERIMENTAL

STARTING MATERIAL

The compositional uniformity of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy samples used in the investigation was $x = 0.2 \pm 0.005$. Most of the experiments were carried out with starting material that was free of macroscopic defects such as precipitates, pores and Hg or Te inclusions; in a few experiments where the intent was to establish the effect of macroscopic defects on the efficiency of quenching the high temperature equilibrium, material with a relatively high density of voids and inclusions was used. In order to assure ourselves that equilibrium was attained at temperatures as low as 400 to 460°C within reasonable annealing periods (2 to 3 weeks), and also to increase the efficiency of quenching the high temperature equilibrium, the thickness of most of the $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ samples used in the present investigation was restricted to ≤ 0.04 cm. The residual donor or acceptor concentration in the starting undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ material was $\leq 10^{16}\text{cm}^{-3}$.

COPPER DOPING

Doping to different concentrations of copper was obtained by evaporating various amounts of copper on to the surface of the undoped samples and subsequently diffusing in the copper in a known atmosphere of Hg. Copper concentration obtained in the doped samples was determined by atomic absorption analysis carried out by Photometrics, Inc., Lexington, Massachusetts.

It is to be noted that the samples used for copper diffusions at temperatures below 400°C had been previously annealed at 250°C for several months in order to reduce the native acceptor defect concentration to less than 10^{15}cm^{-3} . Since copper has a high diffusivity in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys [6-7], diffusion times of 6 to 8 weeks were found adequate for uniform doping of samples (0.04 cm thick) at temperatures below 400°C; uniform doping at these temperatures was confirmed by sequentially lapping away the material from both sides of the samples and making certain that the hole concentrations did not change.

PHOSPHORUS DOPING

The phosphorus doped samples used in the present work were obtained from a phosphorus doped ingot grown at Honeywell using the quench/anneal technique [8].

HIGH TEMPERATURE ANNEALING

Prior to the anneals, crystals were cleaned in organic solvents followed by a Br-methanol etch and a final rinse in DI water. Annealing experiments in various partial pressures of Hg were carried out in evacuated quartz ampoules containing a small amount of Hg also, to obtain the desired Hg vapor pressure. In those experiments where the desired Hg pressure was high enough, an isothermal setup was used where the free Hg and the $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ samples were kept at the same temperature; the vapor pressure of Hg in such a set up depended on the amount of free Hg in the ampoule and the volume of the ampoule. In experiments where the desired Hg pressure was low, a two temperature zone set up was used; the $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals were kept at the higher temperature end of the ampoule and the free Hg at the lower temperature end; the vapor pressure of Hg obtained corresponded to the saturation pressure of Hg at the lower temperature and was independent of the amount of Hg in the ampoule. The limits of Hg pressure -- within which the solid is stable at a given temperature -- were obtained from the partial pressure - temperature data for HgTe [9] and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys [10-11].

Equilibration periods ranging from 16 to 24 hours were used for annealing at temperatures of 500°C or greater and a two week equilibration was used for annealing temperatures of 460°C and 400°C. Subsequent to the anneals, the samples were rapidly quenched in ice water, to freeze in as much of the high temperature equilibrium as possible; in a few cases the samples were air cooled from the equilibration temperatures.

ELECTRICAL MEASUREMENTS

Hall effect and resistivity measurements were made using the van der Pauw method [12]. Magnetic field strengths of 400 Gauss and 4000 Gauss were used for the measurement of the Hall coefficient.

RESULTS

Only those Hall coefficient measurements where the Hall coefficient R_H did not vary with varying magnetic field strength, (400 G to 4000 Gauss) were used in evaluating the hole concentrations in the crystals. This ensured that the samples did not show mixed conduction [13] and the carrier concentration was given by:

$$\frac{1}{|R_H|q}$$

Figure 1 shows the variation of the Hall coefficient as a function of the temperature of measurement for the undoped samples equilibrated at different temperatures under known partial pressures of Hg and quenched to room temperature. It is evident from the figure that at temperatures exceeding 145 K the contribution from the intrinsic carriers becomes important, whereas, at temperatures between 77 K and 145 K the Hall coefficient is temperature independent indicating that the native acceptors are completely ionized at 77 K for concentrations ranging from 10^{17} cm^{-3} to 10^{18} cm^{-3} . Based on this inference, all the Hall effect measurements on the undoped samples were carried out at 77 K and the resulting hole concentration was assumed to give a measure of the native acceptor defect concentration incorporated at the higher equilibration temperatures.

Figure 2 shows the hole concentrations at 77 K as a function of the partial pressure of Hg for the undoped crystals annealed at various temperatures and quenched to room temperature. The samples are invariably p-type for all partial pressures of Hg (throughout the existence region) at temperatures greater than 400°C and the hole concentration is roughly inversely proportional to the partial pressure of Hg, p_{Hg} . Phase boundary limits at each temperature are indicated by arrows in the figure. The solid lines shown in the figure correspond to the hole concentrations calculated on the basis of the defect model for the undoped crystals, to be discussed later.

Figure 3 shows the variation of the Hall coefficient as a function of the temperature of measurement for crystals doped with different copper concentrations. Just as with the undoped crystals, most of the copper present in the

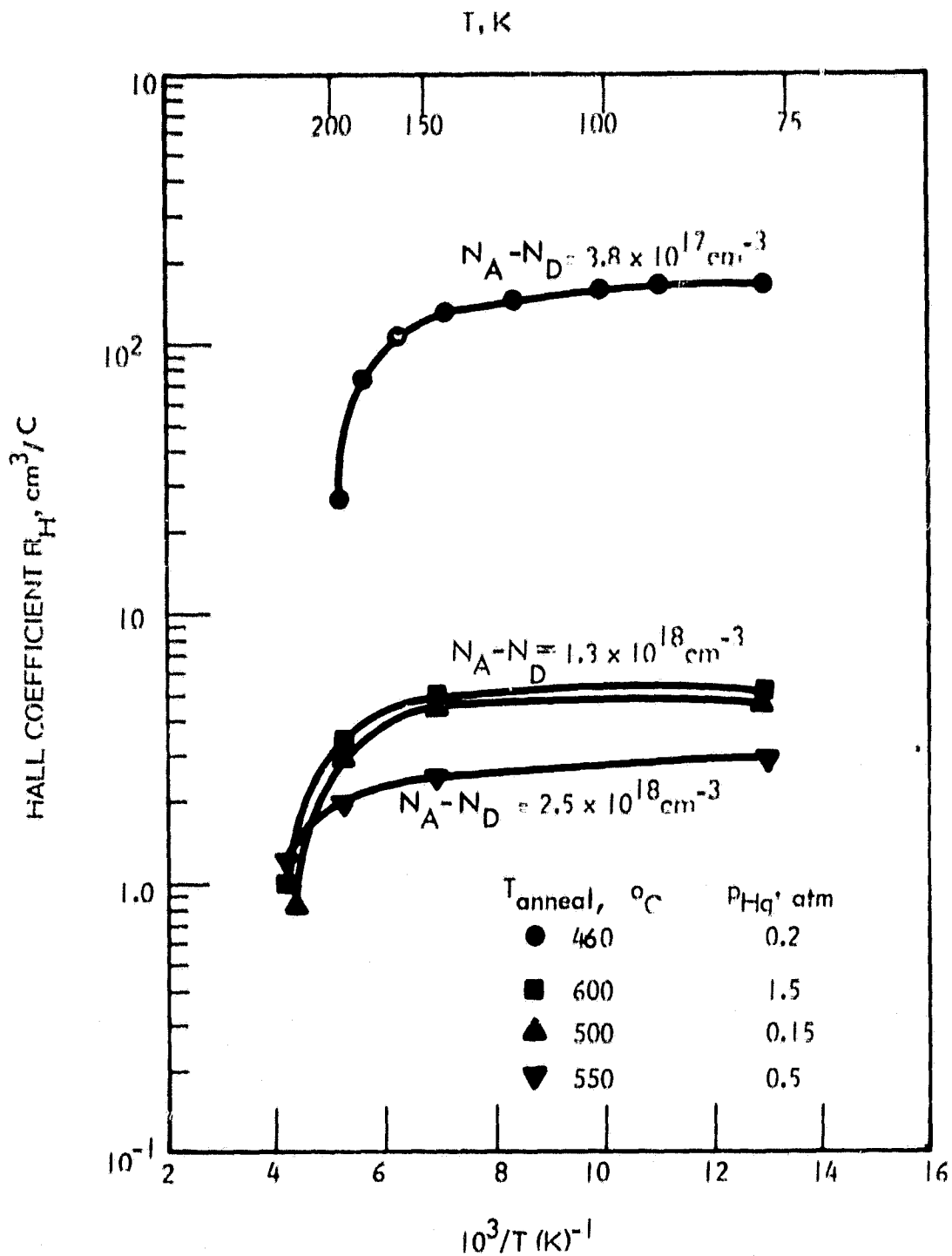


Figure 1: Hall coefficient as a function of measurement temperature for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ samples equilibrated at the indicated temperatures and partial pressures of Hg and quenched to room temperature.

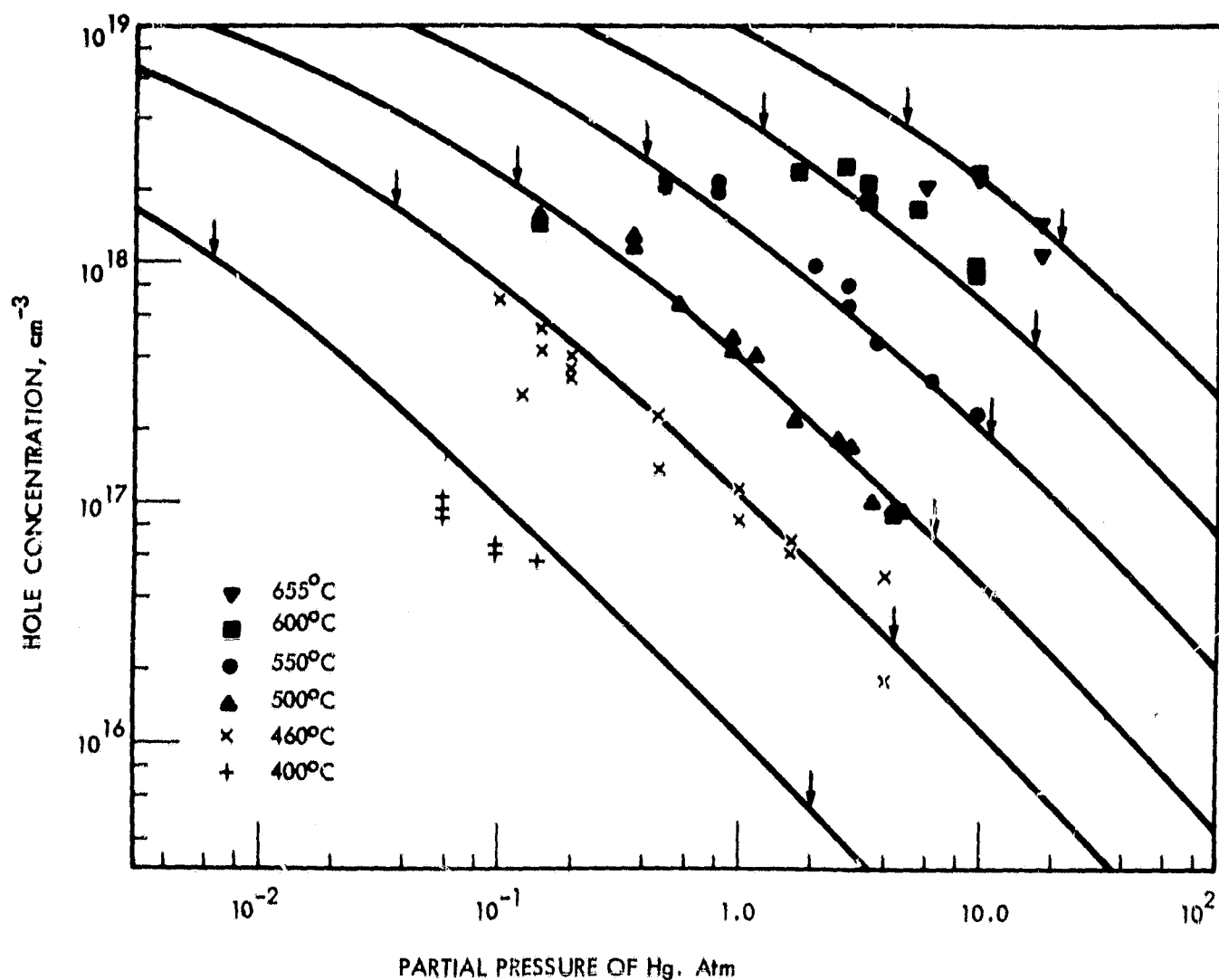


Figure 2: Hole concentration at 77 K as a function of the partial pressure of Hg for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}$ crystals annealed at various equilibration temperatures and quenched to room temperature; solid lines correspond to the values calculated on the basis of the defect model discussed in the text.

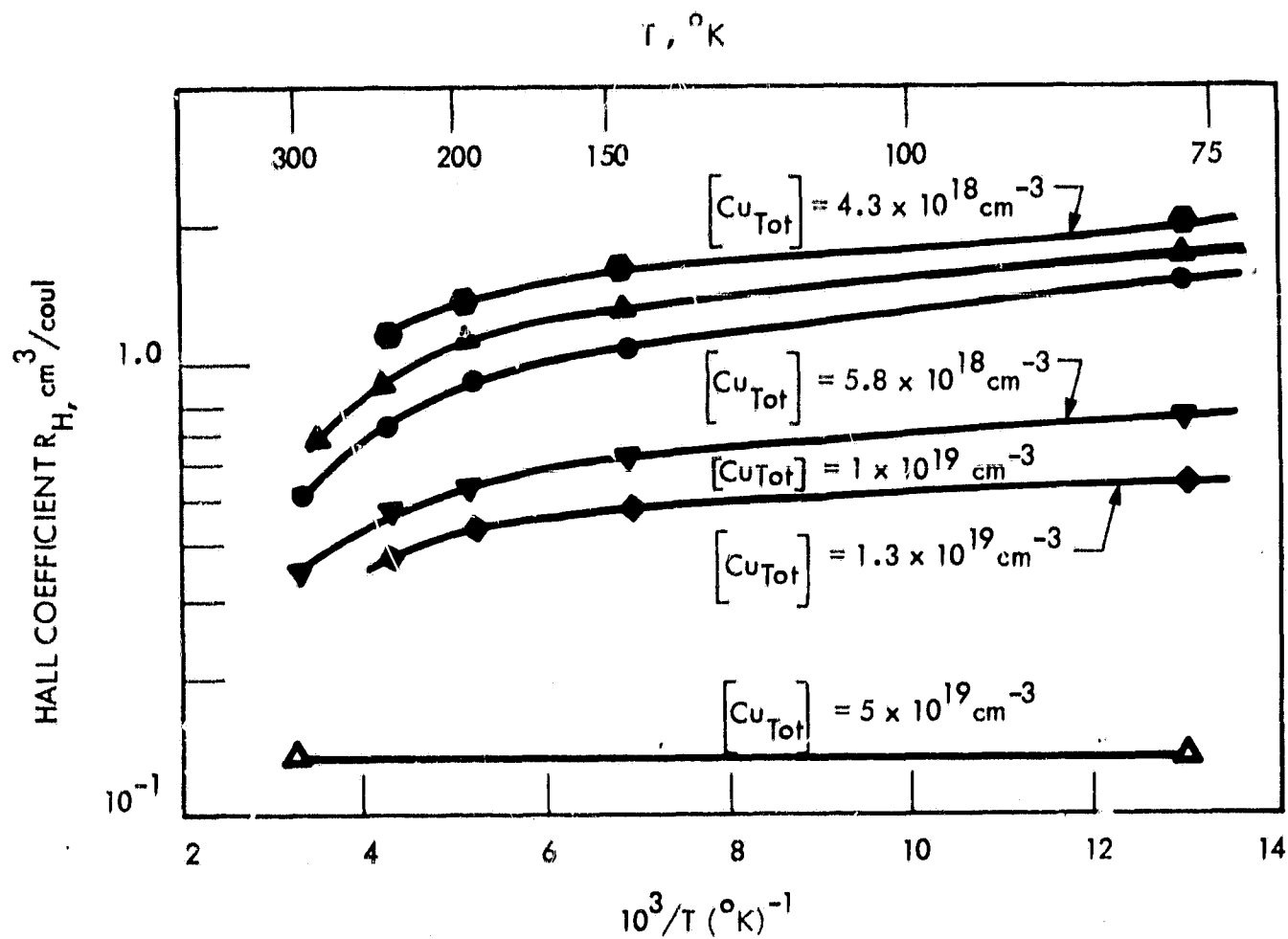


Figure 3: Hall Coefficient as a function of measurement temperature for copper doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals.

electrically active form appears to be completely ionized between 77 K and 145 K and at temperatures greater than 145 K the contribution from the intrinsic carriers becomes significant. The total amount of the electrically active copper concentration in the samples was inferred from the hole concentrations obtained at 145 K.

Figure 4 shows the hole mobility at 77 K for the undoped crystals as a function of the hole concentration. The data indicate that the hole mobility decreases with increase in hole concentration. Figure 5 shows the hole mobility at 77 K in various copper doped samples as well as in some phosphorus doped samples. The temperatures at which the various copper diffusions were done are also indicated in the figure. It is apparent from Figures 4 and 5 that the copper doped and the phosphorus doped samples have higher hole mobilities than the undoped samples containing similar hole concentrations.

Figure 6 shows the hole mobility and hole concentration in a phosphorus doped sample annealed at 550°C under various partial pressures of Hg. Figure 7 shows similar data for an undoped crystal. The data in Figures 6 and 7 indicate that, although the hole concentration in the phosphorus doped sample is relatively independent of the partial pressure of Hg, the hole mobility increases with increase in the partial pressure of Hg (Figure 6) just as is observed in the undoped crystal (Figure 7).

Figure 8 compares the electrical conductivity at 77 K obtained in the undoped crystals containing a relatively large concentration of voids and inclusions (~ 1000 per cm^2) with those containing a negligible concentration of these (≤ 20 per cm^2) subsequent to anneals at 500°C in different partial pressures of Hg and air cooled or quenched to room temperature; the voids and inclusions in the samples were approximately 10 to 30 μm in diameter, and depending on how the bulk crystals were grown, the inclusions were either Hg rich or Te rich. Figure 9 shows the electrical conductivity at 77 K, obtained in the undoped crystals containing a large concentration of voids and inclusions and which were air cooled to room temperature subsequent to anneals at 500°C in different partial pressures of Hg. Figures 8 and 9 clearly show that

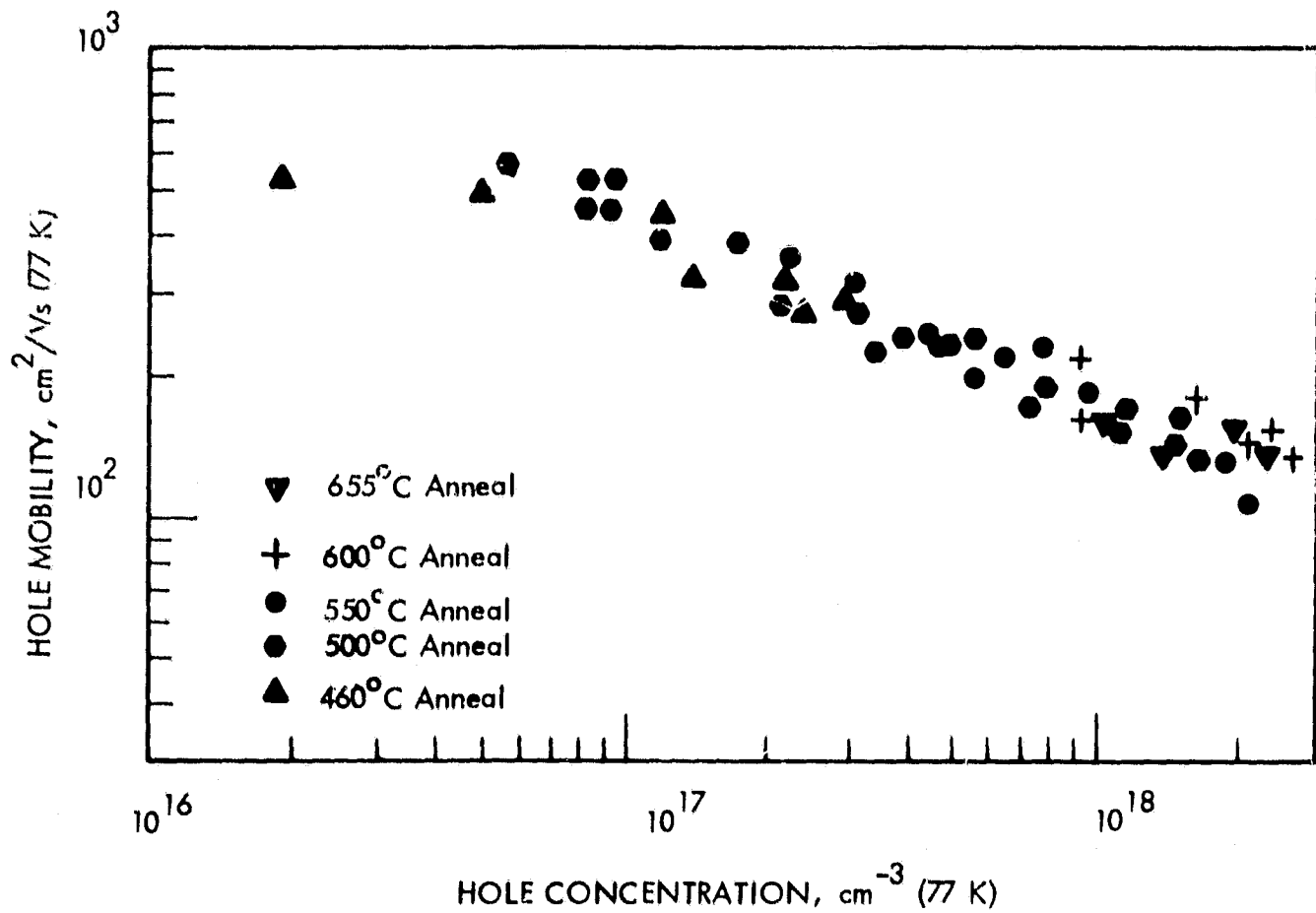


Figure 4: Hole mobility at 77 K as a function of hole concentration for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals.

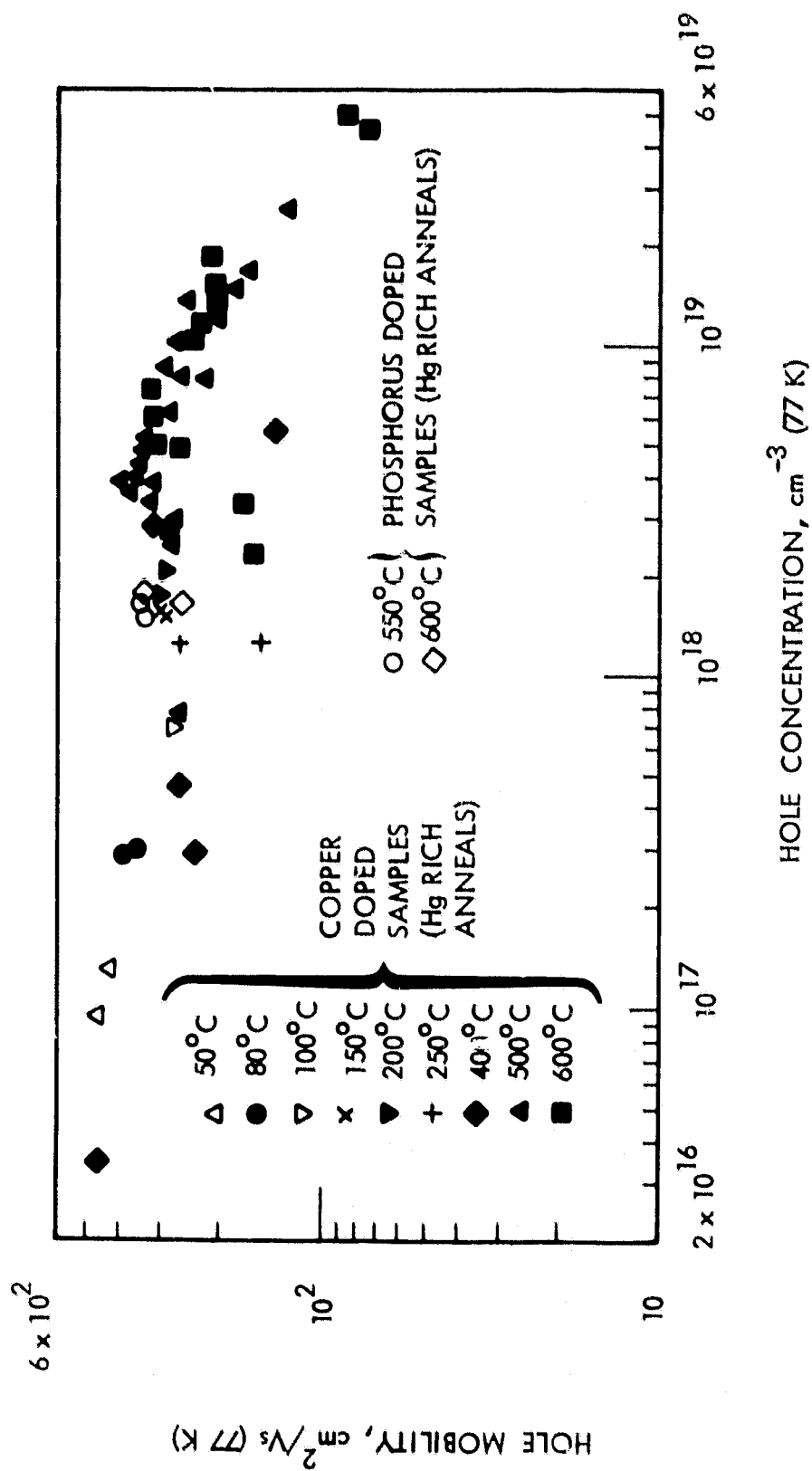


Figure 5: Hole mobility at 77 K as a function of hole concentration for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals doped with various copper concentrations at the indicated temperatures; hole mobility for a few phosphorus doped samples is also shown.

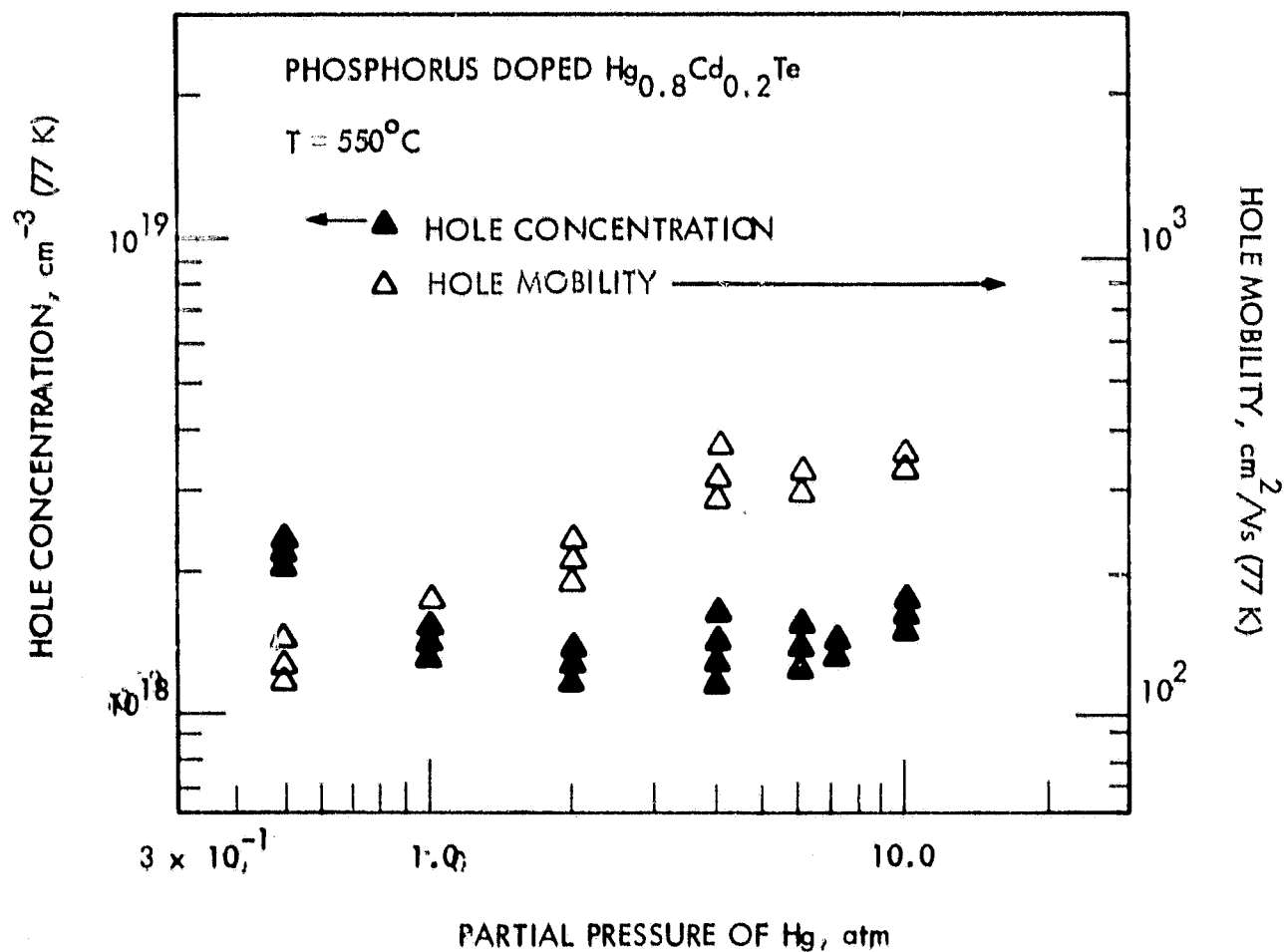


Figure 6: Hole concentration and hole mobility as a function of the partial pressure of Hg for a phosphorus doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ sample annealed at 550°C and quenched to room temperature.

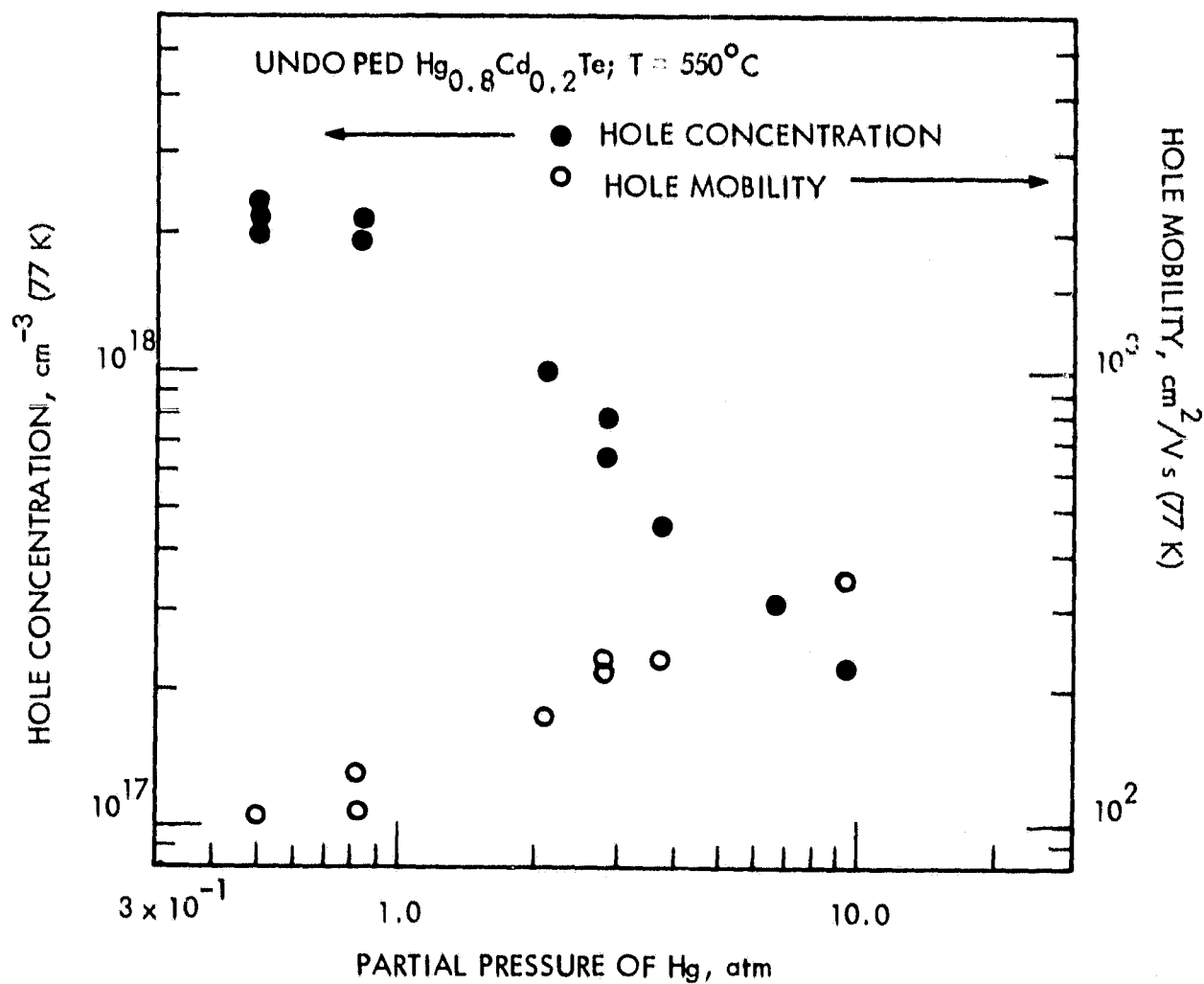


Figure 7: Hole concentration and hole mobility at 77 K as a function of the partial pressure of Hg for an undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ sample annealed at 550°C and quenched to room temperature.

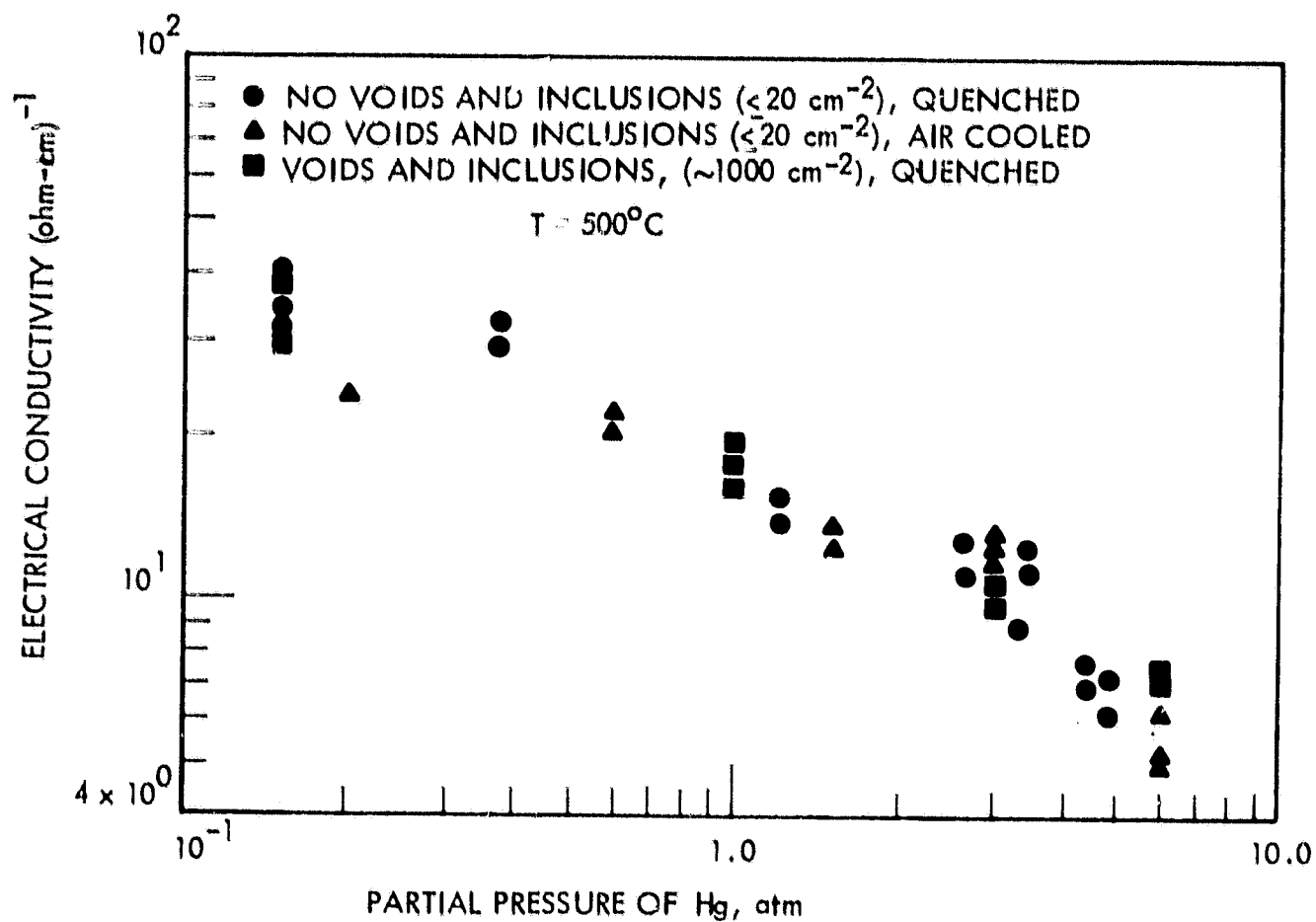


Figure 8: Electrical conductivity at 77 K for various sets of undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals containing different concentrations of voids and inclusions and quenched or air cooled subsequent to anneals in different Hg pressures at 500°C.

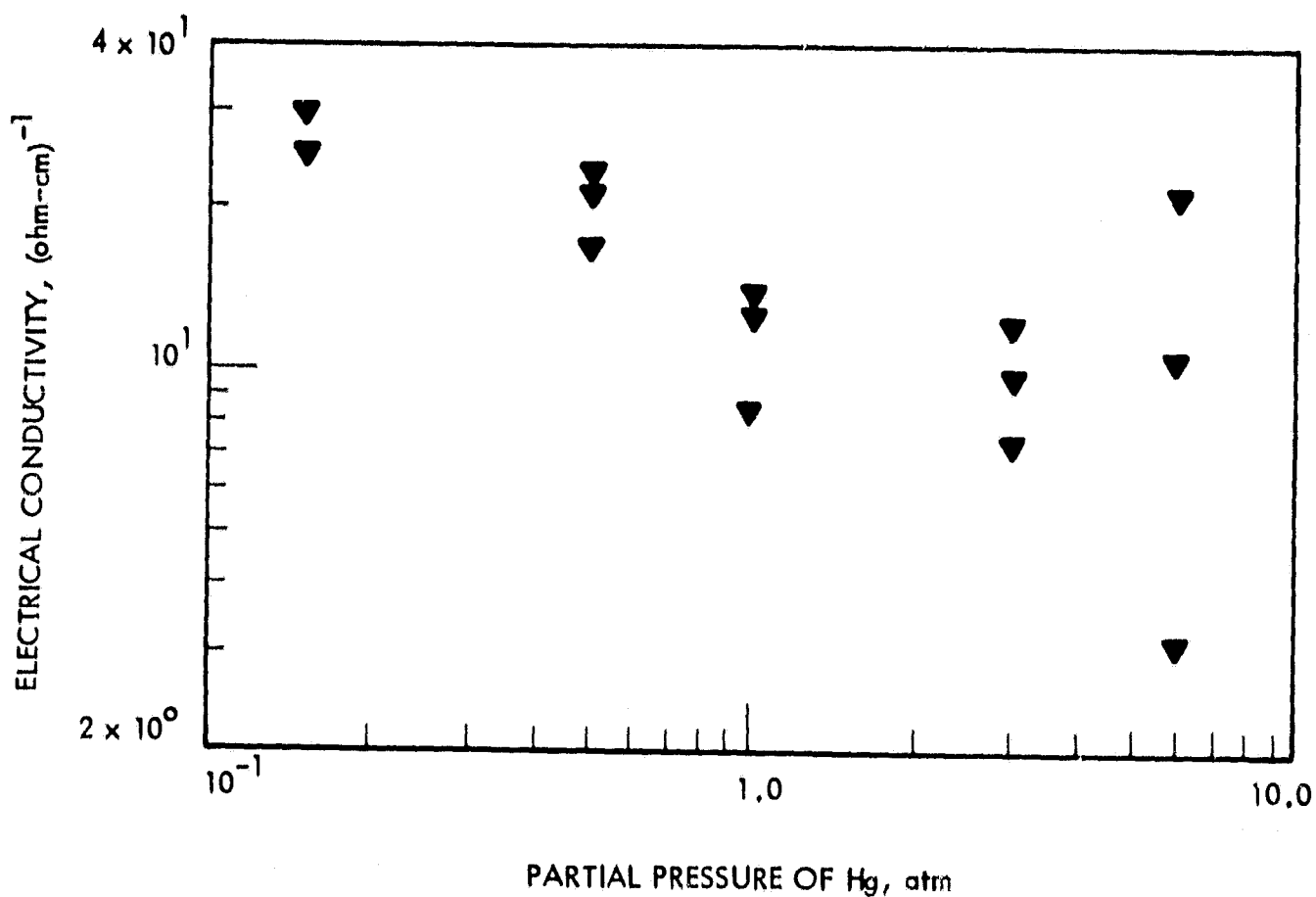


Figure 9: Electrical conductivity at 77 K for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals containing a large concentration of voids and inclusions and air cooled subsequent to anneals in different Hg pressures at 500°C.

the electrical conductivity variations as a function of the partial pressure of Hg are similar for undoped crystals with and without voids and inclusions that were quenched to room temperature subsequent to equilibration at 500°C ; the results are also similar for the undoped crystals containing virtually no voids and inclusions and which were air cooled from 500°C . However, considerable scatter is obtained in the results for the undoped crystals containing a large concentration of voids and inclusions and which were air cooled from 500°C .

DISCUSSION

DEFECT EQUILIBRIA

The way in which the concentrations of defects vary as a function of the physicochemical conditions of preparation (temperature, partial pressure of Hg or partial pressure of Te_2 and/or the dopant concentration) can be arrived at by utilizing the quasichemical approach developed by Kröger and Vink [14]. The quasichemical approach has been used in many binary compounds to establish defect models [15]. In such an approach, atomic and electronic defects are considered as chemical species and defect formation reactions along with the corresponding mass action relations are formulated. The concentrations of all the defect species comprising the electroneutrality condition and the dopant balance equation (for the doped crystals) are then expressed in terms of the relevant mass action constants and the concentration of one defect species. This results in equations containing the various mass action constants and the concentrations of one single defect species; numerical solution will then yield the concentration of this defect species for given values of the mass action constants. Once the concentration of one defect species is determined the concentrations of all the other defect species can be evaluated via the mass action relations.

Defect formation reactions and mass action relations for various defect species are listed in Table 1. The defect notations are according to the scheme of Kröger and Vink [14], in which the major symbol indicates the defect, the subscript denotes the type of lattice site occupied and the

Table 1. LIST OF THE DEFECT FORMATION REACTIONS, MASS ACTION CONSTANTS, ELECTRONEUTRALITY CONDITION AND DOPANT BALANCE EQUATION

Reaction	Mass Action Relation
1. $0 \longrightarrow e' + h^{\bullet}; E_f$	$K_i = [e'] [h^{\bullet}]$
2. $Hg^X_{Hg} \longrightarrow V''_{Hg} + 2h^{\bullet} + Hg(g); H''_{VHg}$	$K''_{VHg} = [V''_{Hg}] [h^{\bullet}]^2 p_{Hg}$
3. $V^X_{Hg} \longrightarrow V'_{Hg} + h^{\bullet}; E_{a1V}$	$K_{a1V} = [V'_{Hg}] [h^{\bullet}] / [V^X_{Hg}]$
4. $V'_{Hg} \longrightarrow V''_{Hg} + h^{\bullet}; E_{a2V}$	$K_{a2V} = [V''_{Hg}] [h^{\bullet}] / [V'_{Hg}]$
5. $(Hg_{0.8Cd0.2}Te) (S) \longrightarrow 0.8 Hg(g) + 0.2 Cd(g) + 1/2 Te_2(g); H_{Hg0.8Cd0.2Te}$	$K(Hg_{0.8Cd0.2}Te) = p_{Hg}^{0.8} p_{Cd}^{0.2} p_{Te_2}^{1/2}$
6. $0 \longrightarrow V''_{Hg} + V''_{Te}; H''_s$	$K''_S = [V''_{Hg}] [V''_{Te}]$
7. $Hg^X_{Hg} \longrightarrow V''_{Hg} + Hg_i^{\bullet}; H''_F$	$K''_F = [V''_{Hg}] [Hg_i^{\bullet}]$
8. $Hg(l) \longrightarrow Hg(g); H_{Hg}$	$K_{Hg} = p_{Hg} / a_{Hg}$
9. $Te(l) \longrightarrow 1/2 Te_2(g); H_{Te}$	$K_{Te} = p_{Te_2}^{1/2} / a_{Te}$
10. Electroneutrality condition:	
	$[e'] + [Cu'_{Hg}] + [V'_{Hg}] + 2[V''_{Hg}] = [h^{\bullet}] + [Cu_i^{\bullet}] + [Hg_i^{\bullet}] + 2[Hg_i^{\bullet}] + 2[V''_{Te}]$
11. Copper balance equation:	
	$[Cu'_{Hg}] + [Cu_i^{\bullet}] = [Cu_{tot}]$

superscript indicates the charge. Superscripts dash (') and dot (•) stand for effective negative and positive charges respectively, while a cross (x) stands for a neutral charge. Thus V''_{Hg} indicates a doubly negatively ionized vacant lattice site of Hg. Square brackets indicate concentrations expressed as site fractions. The native acceptor defect species considered in this paper are the vacancies of Hg instead of the interstitials of Te. Electrical measurements cannot distinguish between the two species and hence the results will be the same if interstitials of Te are considered as the native acceptor defect species instead. Recent work on the defect structure of CdTe [16,17] determined by Hall effect and tracer self-diffusion data indicates the presence of appreciable concentrations of Te interstitials also in addition to the vacancies of Cd. Although the results of the present work showed no evidence of presence of any native donor defects such as Hg_i or V_{Te} , etc., in any appreciable concentration, Table 1 includes these defects also, for purposes of later discussions in the paper.

DEFECT STATE IN THE COOLED CRYSTALS

Ideally, in situ high temperature physical property measurements and measurements on the crystals quenched from the equilibration temperatures should both be used to arrive at defect states prevailing at the high temperature as well as in the cooled crystals; much information regarding precipitation of atomic defects during quenching can be obtained by correlating the defect state in the cooled crystals with that obtained at the equilibration temperatures. CdTe [16-20] is only one of the few materials that has been studied extensively from such a viewpoint. In the present work however, the defect state in the cooled crystal shall be used to derive information regarding the defect state prevailing at the equilibration temperatures.

While attempting to deduce the high temperature defect state of the crystals from measurements on the crystals quenched to room temperature from the high temperature physicochemical conditions, a few assumptions are made. The assumptions are that (1) the electrons and the holes recombine during cooling, that (2) all the atomic defects at the high temperature are frozen in and that (3) the intrinsic carrier concentration $n_i = K_i^{1/2}$ at the

measurement temperature \ll concentration of the electrically active atomic defects so that the Fermi level is pinned at the defect level and the carrier concentration in the cooled crystals gives the concentration of the atomic defects corresponding to the high temperature equilibrium. The first assumption is always satisfied and the third one is also satisfied as long as the carrier concentration measurement temperature is low enough for n_i to be low. The second assumption requires that the crystals be quenched fast enough that the precipitation of the atomic defects is not given risen to.

APPROXIMATION TO THE ELECTRONEUTRALITY CONDITION AND DOPANT BALANCE CONDITION

When the electroneutrality condition and the dopant balance equation (Table 1) are approximated by only the dominant members [21] one can obtain the variation of the defect concentrations as a function of p_{Hg} and the total copper concentration (for copper doped crystals) in the form

$$\text{Concentration} \propto p_{Hg}^r [Cu_{tot}]^s$$

where r and s are small integers or fractions.

Table 2 lists the exponents of p_{Hg} and cu_{tot} for the variation of the concentrations of the different defects for various approximations to the electroneutrality condition.

NATIVE ACCEPTOR DEFECTS

The fact that the hole concentration in the undoped crystals is proportional to p^{-1} (Figure 2) indicates that the crystals are essentially intrinsic at the high temperature (Table 2, electroneutrality approximation $[e'] = [h']$); however, as can be noted from Table 2, for a situation, where the crystal is intrinsic, all the native acceptor defects vary as p^{-1} irrespective of the charge state of the defects. In order to establish the charge state of the native acceptor defects dominant in the undoped crystals the electrical characteristics of the undoped and the acceptor doped crystals

Table 2. VARIATIONS OF THE DEFECT CONCENTRATIONS AS A FUNCTION OF P_{Hg} AND/OR COPPER CONCENTRATIONS FOR VARIOUS APPROXIMATIONS TO THE ELECTRONEUTRALITY CONDITION

Type of Defect and Approximation to the Electro- neutrality Condition	$[] \propto P_{Hg}^r [Cu_{tot}]^s$		Cooled Crystals		Hole Concentration in the	
	r	s	r	s		s
1. $[e'] = [h'] = K_i$	0	0				
$[V''_{Hg}]$	-1	0	-1	0		0
$[V'_{Hg}]$	-1	0	-1	0		0
$[Hg_i']$	+1	0	+1	0		0
$[Hg_i'']$	+1	0	+1	0		0
$[V_{Fe}']$	+1	0	+1	0		0
$[Cu'_{Hg}] = [Cu_{tot}]$		1	0	1		1
2. $[Cu'_{Hg}] = [Cu_{tot}] = [h']$	0	1	0	1		1
$[V''_{Hg}]$	-1	-2				
$[V'_{Hg}]$	-1	-1				
$[Hg_i']$	+1	+1				
$[Hg_i'']$	+1	+2				
$[V_{Fe}']$	+1	+2				
3. $[h'] = 2 [V''_{Hg}]$	-1/3	0	-1/3	0		0
$[e']$	+1/3	0				
$[V'_{Hg}]$	-2/3	0				
$[Hg_i']$	+2/3	0				
$[Hg_i'']$	+1/3	0				
$[V_{Fe}']$	+1/3	0				
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1				

Table 2. VARIATIONS OF THE DEFECT CONCENTRATIONS AS A FUNCTION OF P_{Hg} AND/OR COPPER CONCENTRATIONS
FOR VARIOUS APPROXIMATIONS TO THE ELECTRONEUTRALITY CONDITION (Continued)

Type of Defect and Approximation to the Electro- neutrality Condition	$[] \propto P_{Hg}$		r		s		Hole Concentration in the Cooled Crystals
	r	s	r	s	r	s	
4. $[V''_{Hg}] = [V_{Te}^{..}] = K''s$	0	0					
$[e']$	1/2	0					
$[h^{\bullet}]$	-1/2	0					
$[V'_{Hg}]$	-1/2	0					
$[Hg_i^{\bullet}]$	+1/2	0					
$[Hg_i^{..}]$	0	0					
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1					
5. $[V''_{Hg}] = [Hg_i^{\bullet}] = K''F$	0	0					
$[e']$	1/2	0					
$[h^{\bullet}]$	-1/2	0					
$[V'_{Hg}]$	-1/2	0					
$[Hg_i^{\bullet}]$	+1/2	0					
$[V_{Te}^{..}]$	0	0					
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1					

will be compared. Figure 4 shows that the hole mobilities in the undoped crystals at 77 K decrease with increase in the hole concentration indicating that the contribution of ionized impurity scattering to the hole mobilities is substantial. If so, the fact that a majority of the copper doped crystals shown in Figure 5 have higher mobilities than the undoped crystals indicates that the ionized impurity scattering is less in the copper doped crystals; the results can be explained if copper is a single acceptor occupying Hg lattice sites and the native acceptor defects in the undoped crystals are doubly ionized. Based on the theory of ionized impurity scattering [22], for comparable hole concentrations, the mobilities due to ionized impurity scattering in the copper doped crystals containing x number of singly ionized copper centers can be expected to be twice that in the undoped crystals containing $x/2$ number of the doubly ionized native acceptor defect centers. Also, in those crystals where the electrically active copper concentration exceeds the intrinsic carrier concentration at the annealing temperatures, thus extrinsically doping them, the native acceptor defect concentration decreases with increase in the copper concentration as a consequence of the mass action effect. As can be seen from Table 2, as soon as the crystals become extrinsic with copper doping and the electroneutrality approximation becomes $[Cu'Hg] = [h^*]$, the doubly ionized native acceptor defects decrease proportional to the square of the copper concentration in the crystals ($[V''Hg] \propto [Cu_{tot}]^{-2}$). This is shown schematically in Figure 10. Hence, in samples doped with copper to greater than the intrinsic carrier concentration, the concentration of the doubly ionized native defects is considerably depressed. If the native acceptor defects were singly ionized, their concentration would decrease inversely linearly proportional to $[Cu_{tot}]$ as soon as the copper concentration exceeds the intrinsic carrier concentration (Table 2 and Figure 10); however, the hole mobility of such samples should be no different from that of the undoped crystals for comparable hole concentrations. It may be argued that the larger hole mobility in the heavily copper doped samples (Figure 5) may result from shorting paths due to high concentrations of copper; however the fact that the hole mobility in the copper doped samples decreases for hole concentrations in excess of 10^{19} cm^{-3} (Figure 5) rules out this explanation. It should also be noted from Figures 4 and 5 that the hole mobilities are essentially the same for both the copper

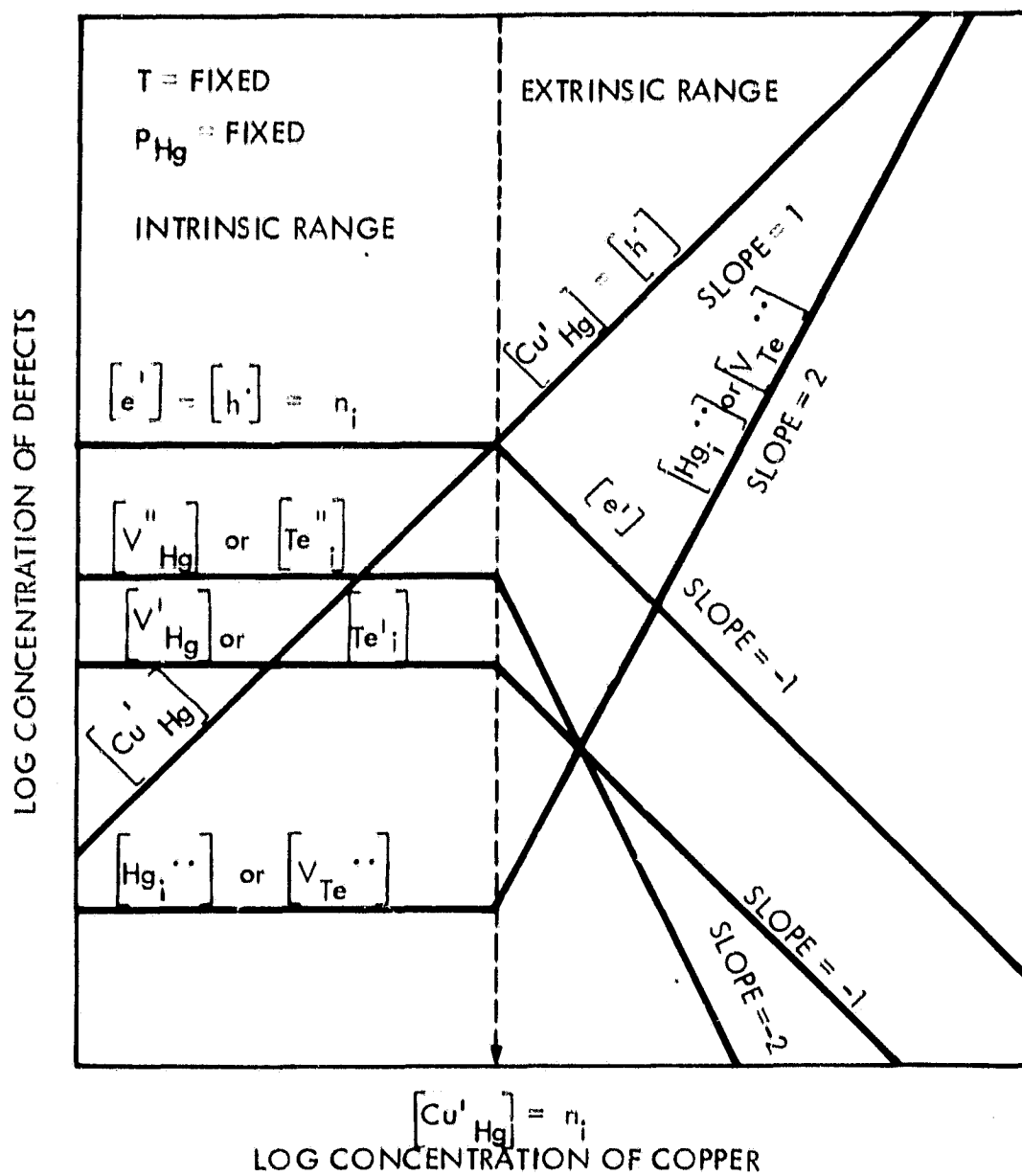


Figure 10: Schematic variation of $[e']$, $[h']$, $[\text{Cu}'_{\text{Hg}}]$, $[\text{V}''_{\text{Hg}}]$ (or $[\text{Te}''_i]$), $[\text{V}'_{\text{Hg}}]$ (or $[\text{Te}'_i]$) and $[\text{Hg}_i^{\bullet\bullet}]$ (or $[\text{V}^{\bullet\bullet}_{\text{Te}}]$) as a function of the electrically active copper concentration in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ at a fixed temperature and partial pressure of Hg.

doped and the undoped samples when the hole concentration is less than 10^{17} cm^{-3} . This result indicates that ionized impurity scattering is probably less significant for hole concentrations less than 10^{17} cm^{-3} . Although the expression for ionized impurity scattering [22] predicts larger mobilities for the copper doped samples than for the undoped samples for comparable hole concentrations, the results of Figure 5 indicate that the hole mobility for a majority of the copper doped samples --- containing electrically active copper concentration between 10^{18} to 10^{19} cm^{-3} --- appears to be larger than can be accounted for by the Brooks-Herring expression [22] alone. Hole mobility calculations based on lattice scattering as well as ionized impurity scattering are needed to explain the data of Figures 4 and 5 quantitatively [23].

Hole mobility data in phosphorus doped crystals provide additional evidence for the argument that the native acceptor defects are doubly ionized. The fact that the phosphorus doped samples in Figure 5 have hole mobilities comparable to the copper doped crystals and higher than the undoped crystals for similar hole concentrations indicates that the native acceptor defects are doubly ionized whereas phosphorus is singly ionized. The results of Figures 6 and 7 further substantiate these facts. These figures show that although the hole concentration in the phosphorus doped sample is essentially independent of the partial pressure of Hg, the hole mobility increases with increase in the partial pressure of Hg (Figure 6) just as for the undoped crystals (Figure 7). This inference can be explained only on the basis that phosphorus is singly ionized, the native acceptor defects are doubly ionized and the electrically active phosphorus concentrations of $1.5 \times 10^{18} \text{ cm}^{-3}$ is insufficient to make the crystals extrinsic at 550°C ; if the crystals are not extrinsic, the doubly ionized native acceptor defect concentration in the phosphorus doped crystals remains the same as in the undoped crystals and varies inversely linearly with increase in the partial pressure of Hg just as in the intrinsic undoped crystals (Figure 7). Since the doubly ionized native acceptor defects can be expected to be stronger scattering centers than the singly ionized phosphorus centers, the mobility due to ionized impurity scattering in both the phosphorus doped samples (Figure 6) as well as the undoped samples (Figure 7) is influenced essentially by the doubly ionized native acceptor defects and thus the hole mobility in both the phosphorus doped samples as well as the undoped samples increases with increase in partial pressure of Hg (Figures 6 and 7).

Details of the defect structure of phosphorus doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ shall be published elsewhere [24]. Figure 11 shows hole concentration and hole mobility as a function of the partial pressure of Hg for a sample containing $1.5 \times 10^{19} \text{ cm}^{-3}$ electrically active copper. The sample shown in Figure 11 is doped with copper concentrations high enough to make it extrinsic at 500°C and thus depressing the doubly ionized native acceptor defect concentration considerably enough that the hole concentration and mobility are totally dominated by copper, unlike the phosphorus doped sample of Figure 6 where the crystal is not extrinsic.

Assuming that the native acceptor defects are doubly ionized in $\text{Hg}_{0.8}\text{Cd}_{0.4}\text{Te}$ also, electrical data in $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ have been analyzed by us in a separate paper [25].

ABSENCE OF COMPENSATION IN THE UNDOPED AND COPPER DOPED CRYSTALS

Absence of compensation in the undoped as well as the copper doped crystals of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ is evidenced by a few inferences. First, the hole mobilities in the undoped crystals are only dependent on the hole concentration and are independent of the temperature of anneal; if there was any compensation by native defects, the concentration of these defects would be expected to be exponentially dependent on temperature and the mobility dependence on the hole concentration would not have been nearly as linear as shown in Figure 4. Second, if the undoped crystals had a considerable concentration of native donor defects compensating the native acceptor defects the concentration of these native donor defects would have considerably increased via the mass action effect as soon as the copper concentration exceeded the intrinsic carrier concentration and the crystal became extrinsic (Table 2 and Figure 10). Since the copper doped crystals, in fact, have higher mobilities than the undoped crystals for comparable hole concentrations, the undoped and the copper doped crystals seem to be uncompensated and the native donor defect concentration in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ seems to be negligible. Absence of compensation has been established in $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$, also [25].

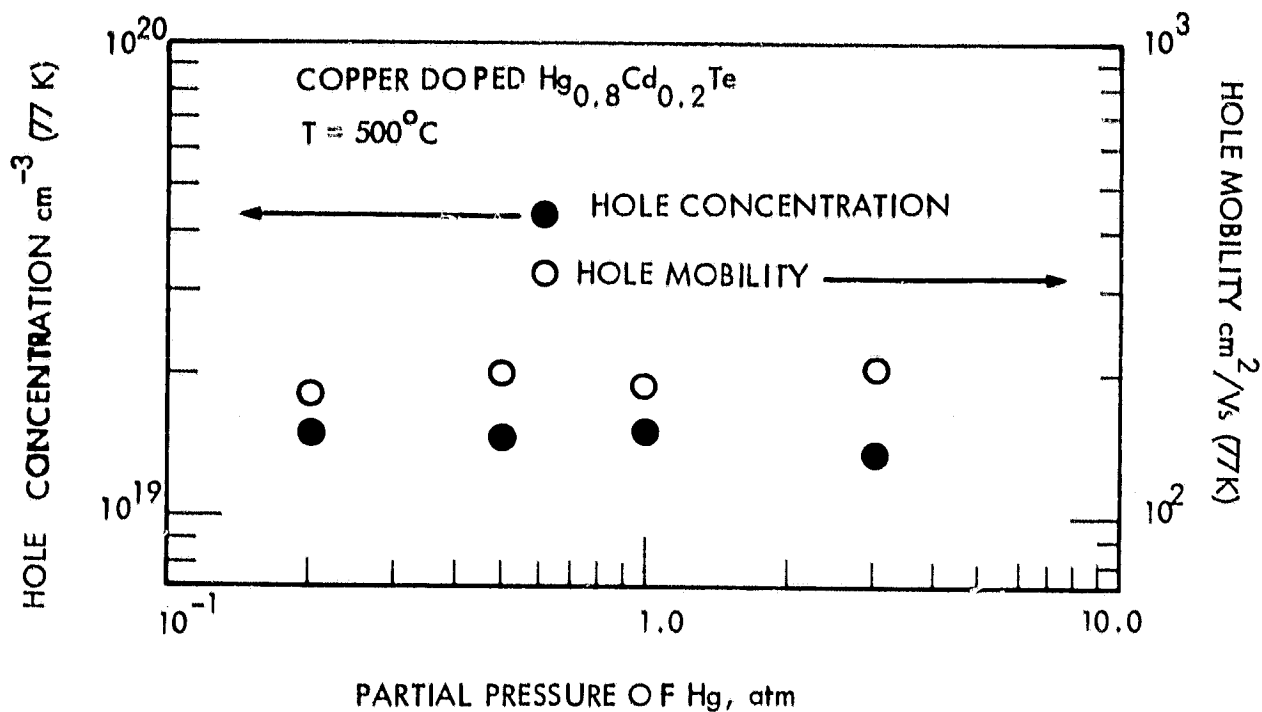


Figure 11: Hole concentration and hole mobility at 77 K as a function of the partial pressure of Hg at 500°C for a sample containing $1.5 \times 10^{19} \text{ cm}^{-3}$ of electrically active copper.

ORIGIN OF p-type TO n-type CONVERSION

In the absence of any systematic defect studies in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ various reasons for p-type to n-type conversion have been proposed [2-5,26,27]. Reynolds et al [26] observed that the $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals annealed under Hg saturated conditions converted to n-type below 360°C and the electron concentration was independent of temperature of anneal below 360°C . The temperature independence of the electron concentration under Hg saturated conditions led them to conclude that the n-typeness was due to residual donors in the crystals and not due to any native donor defects. Similar inferences and conclusions were reported recently by Bartlett et al [27] for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$. Schmit and Stelzer [28] observed that their undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ samples also turned n-type at temperatures below 350° to 400°C under Hg saturated conditions. Also the conversion temperatures were different for different samples. Although the temperature independence of the electron concentration in the undoped crystals of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ [26,27] and $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ [28] for Hg saturated conditions, does not, by itself, rule out the n-type conversion to be due to native donor defects (see appendix) the fact that the different samples in the experiments of Schmit and Stelzer [28] converted to n-type at different temperatures indicates that the conversion in these samples was due to residual foreign donors in the crystals, the samples with a higher residual foreign donor concentration being able to convert to n-type at a higher temperature. Also it was noticed in the present work that certain of the p-type samples (10^{15} - 10^{16} cm^{-3}) did not convert to n-type even when annealed in Hg saturated conditions at temperatures below 350°C . If the n-type conversion occurs due to native donor defects the inability to convert some of these samples is difficult to explain. In these samples the residual acceptor impurity concentration exceeded the residual donor impurity concentration and hence p-type to n-type conversion was not possible at any temperature. These arguments support our conclusion in the previous section that the native donor defects in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ are negligible in concentration. (Probably much less than 10^{15} cm^{-3} at 350 - 400°C). The n tyneness in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$, as well as $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ does not appear to be due to native donor defects. The assumption that the p-type to n-type conversion in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys occurs due to native donor defects appears erroneous [2-5], and such a conversion occurs only

due to residual donor impurities; also the conversion is only possible for samples with residual donor impurity concentration exceeding the residual acceptor impurity concentration in the crystals.

CORRELATION OF THE QUENCHING EFFICIENCY WITH THE PRESENCE OF VOIDS AND INCLUSIONS

Results of Figures 8 and 9 indicate that the electrical conductivity variations in the cooled crystals at 77 K as a function of the partial pressure of Hg at the equilibration temperatures can be a sensitive function of the cooling rate, particularly for samples containing a large concentration of voids and inclusions (~ 1000 per cm^2). For samples containing a relatively small concentration of voids and inclusions (≤ 20 per cm^2) the results are approximately the same except under very low Hg pressures where the air cooled samples have smaller electrical conductivity than the quenched samples (Figure 8). Electrical conductivity, rather than hole concentration, has been plotted in Figures 8 and 9 for ease of comparison of the results of different anneals; for instance, some of the air cooled samples showed mixed conductivity due to the formation of thin n-type inversion layers formed by a reduction in the hole concentration due to precipitation of native acceptor defects during cooling and/or partial type conversions of the samples. When such layers are thin, the overall conductivity is still dominated by holes ($p\mu_p > n\mu_n$) even if the Hall coefficient is negative ($n\mu_n^2 > p\mu_p^2$) and, hence, electrical conductivity for such samples was assumed to reflect the bulk crystal properties better than the Hall effect results. It can be inferred from Figures 8 and 9 that the cooling rate obtained from air cooling the samples is not high enough to retain the high temperature equilibrium in the samples containing a large concentration of voids and inclusions and, thus, resulting in a reduction of the concentration of the native acceptor defects at 500°C. The diffusion distances for equilibration are lower in the presence of a large concentration of voids and inclusions and, hence, crystals containing a large concentration of these can come to equilibrium at an intermediate temperature between 500°C and room temperature during air cooling, whereas, crystals containing a fewer of them retain the high temperature equilibrium to a greater degree. It should also be noted from Figure 8 that quenching in ice water is fast enough for

crystals containing a large concentration of voids and inclusions to retain the 500°C equilibrium. Although experiments with varying cooling rates were not undertaken at higher temperatures it is reasonable to assume that the effect of the presence of voids and inclusions on the quenching efficiency is greater at temperatures higher than 500°C and lower at lower temperatures.

ANALYSIS OF THE CARRIER CONCENTRATION IN THE UNDOPED CRYSTALS

In the detailed analysis of the carrier concentration in the cooled crystals, the complete electroneutrality condition is considered. In order to distinguish the high temperature state of the crystal from the low temperature state of the crystal (cooled crystals) subscripts HT (high temperature) and LT (low temperature) will be used.

For the undoped crystals knowing that the native acceptor defects are doubly ionized and that the native donor defects are negligible in concentration and neglecting the influence of residual donors and acceptors the complete electroneutrality condition becomes:

$$[e']_{HT} + 2 [V''_{Hg}]_{HT} = [h^\bullet]_{HT} \quad (1)$$

Expressing $[e']$ and $[V''_{Hg}]$ in terms of the mass action constants defined in Table 1, we obtain:

$$(k_i [h^\bullet])_{HT} + 2 (K''_{VHg} [h^\bullet]^2 p_{Hg})_{HT} = [h^\bullet]_{HT} \quad (2)$$

or

$$[h^\bullet]_{HT}^3 - (K_i [h^\bullet])_{HT} = 2 (K''_{VHg} p_{Hg})_{HT}$$

The concentration of holes obtained in the cooled crystals is given by:

$$[h^{\bullet}]_{LT} = 2 [V''_{Hg}]_{HT} = (2 K''_{VHg} [h^{\bullet}]^2 p_{Hg})_{HT}$$

or

$$[h^{\bullet}]_{HT} = (2 K''_{VHg} p_{Hg})_{HT}^{1/2} [h^{\bullet}]_{LT}^{1/2} \quad (3)$$

Combination of (2) and (3) with some simplification gives:

$$\begin{aligned} [h^{\bullet}]_{LT}^{3/2} (2 K''_{VHg} p_{Hg})_{HT}^{1/2} + (K_i)_{HT} [h^{\bullet}]_{LT} \\ = (2 K''_{VHg} p_{Hg})_{HT} \end{aligned} \quad (4)$$

For given values of K_i and K''_{VHg} at various temperatures, the solution of Equation (4) gives the hole concentration in the cooled crystals as a function of p_{Hg} . By a procedure of trial and error, the values of K_i and K''_{VHg} were optimized at each temperature to give the best fit between the experimentally observed hole concentrations and the calculated values. The calculated values are shown in Figure 2 as solid lines. The agreement between the experimental values and the calculations appears to be within limits of experimental error.

Mass Action Constants K_i and K''_{VHg} determined from the present investigation (valid for temperatures between 400°C and 655°C) are given by:

$$K_i = 4.18 \times 10^{-4} \exp (-0.57 \text{ eV/kT}) (\text{Site Fr})^2 \quad (5)$$

and

$$K''_{VHg} = 4.87 \times 10^2 \exp (-2.24 \text{ eV/kT}) (\text{Site Fr})^3 \text{ atm} \quad (6)$$

Noting that there are 1.48×10^{22} molecules/cm³ in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$, we get:

$$K_i = 9.16 \times 10^{40} \exp (-0.57 \text{ eV/kT}) \text{ cm}^{-6} \quad (7)$$

and

$$K''_{VHg} = 1.58 \times 10^{69} \exp (-2.24 \text{ eV/kT}) \text{ cm}^{-9} \text{ atm} \quad (8)$$

Both K_i and K''_{VHg} influence the absolute values of the carrier concentration obtained in the cooled crystals and the variation of the carrier concentration as a function of p_{Hg} . From Table 2, it can be seen that the hole concentration in the cooled crystals (equal to twice the concentration of the doubly ionized native acceptor defects at the anneal temperature) is expected to be proportional to p_{Hg}^{-1} for crystals which are intrinsic, whereas, it is expected to be proportional to $p_{Hg}^{-1/3}$ for crystals which are extrinsic with the situation $[h^*] = 2 [V''_{Hg}]$ at the high temperature. Thus, for a given value of K''_{VHg} , if the chosen K_i value was such that $[V''_{Hg}]$ was comparable in concentration to $[e']$ and $[h^*]$, at the high temperature, the power dependence of the calculated hole concentration in the cooled crystals was between $-1/3$ and -1 . On the other hand, if the chosen K_i values were high compared to the hole concentration in the cooled crystals, the calculated hole concentration varied strictly as p_{Hg}^{-1} . The absolute values of the calculated hole concentrations depended both on K_i and K''_{VHg} . In order to show how sensitive the calculated hole concentrations are to the variation in the K_i values at the anneal temperatures, the hole concentrations in the cooled crystals were calculated as a function of p_{Hg} for K_i values 25% higher and 25% lower than given by the expression 7 for K_i . The calculated hole concentrations in the cooled crystals for K_i values given by the expression as well as for K_i values $\pm 25\%$ are shown for $T = 500^\circ\text{C}$ in Figure 12; the K''_{VHg} value in the calculations was kept constant as given by expression 8. It appears that $\pm 25\%$ variations in K_i do not affect the calculations adversely. Figure 13 plots the K_i values as function of temperature. Sets of lines corresponding to slopes higher and lower than 0.57 eV corresponding to $K_i \pm 0.25 K_i$ are also drawn in the plot. The expression for K_i in terms of semiconductor statistics is written as:

$$K_i = 2 (2\pi m_e m_h kT/h^2)^3 \exp (-E_g/kT) \text{ cm}^{-6}$$

where m_e and m_h are the effective masses of electrons and holes, respectively, and E_g is the energy gap. A positive temperature dependence of the energy gap has been verified by various workers for temperatures up to 300 K [29-32]. To the authors' knowledge, no measurements on the energy gap or the intrinsic carrier concentration at temperatures much in excess of room temperature exist in literature. The most recent empirical expression for the energy

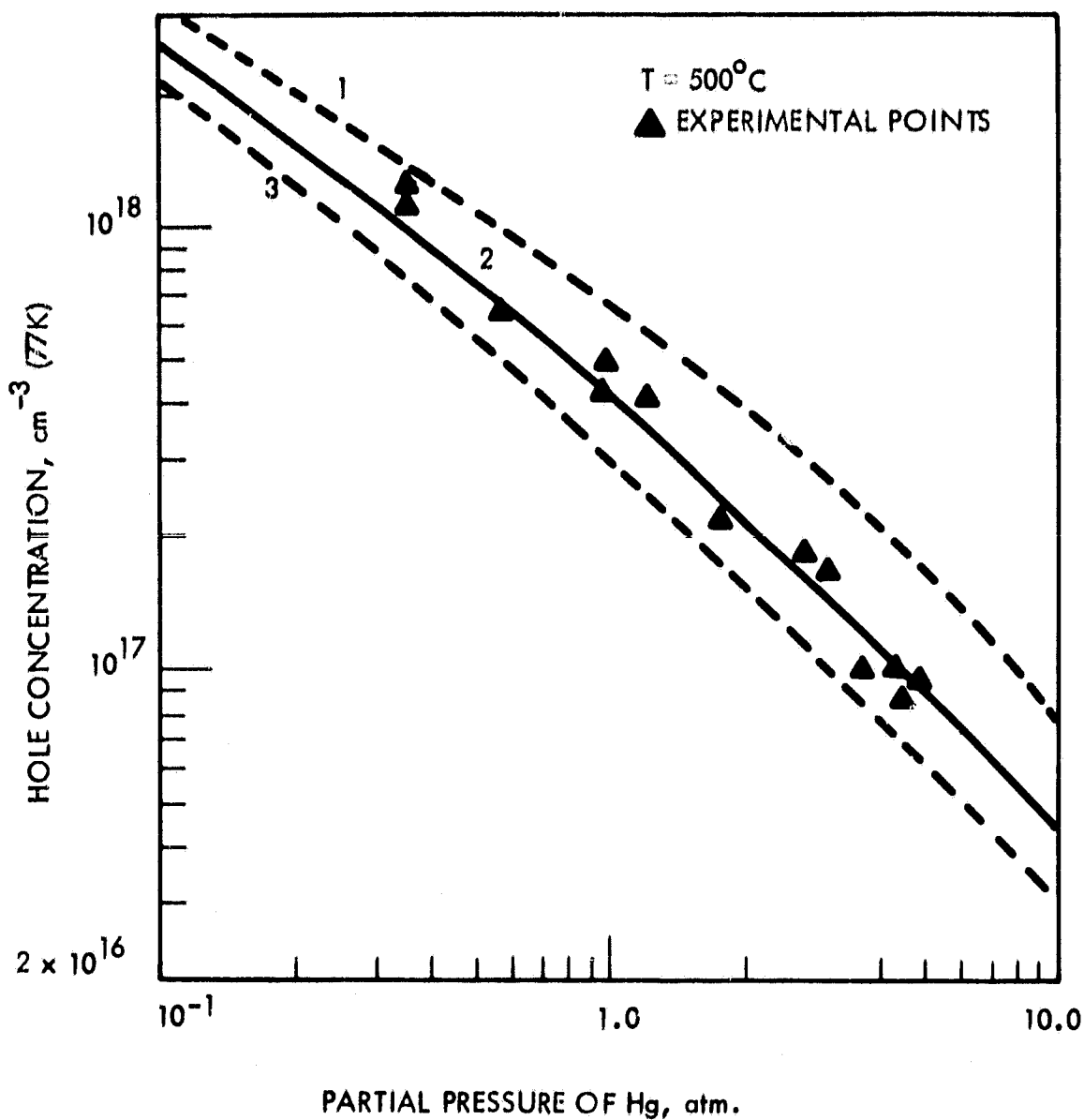


Figure 12: Defect model calculations of the hole concentrations at 77 K for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ annealed at 500°C in various partial pressures of Hg and quenched to room temperature; solid line 2 represents calculations using K_i values given by expression (7) of the text whereas the dashed lines 1 and 3 correspond to calculations using K_i values differing from those of expression (7) by $\pm 25\%$; experimental points are also shown for comparison.

gap dependence on temperature for $x = 0.2$ $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy [32] derived for measurements below room temperature, when extrapolated to higher temperature yields,

$$\begin{aligned} E_g &= 0.3 \text{ eV at } 400^\circ\text{C} \\ \text{and } E_g &= 0.4 \text{ eV at } 655^\circ\text{C} \end{aligned}$$

Taking an average value of 0.35 eV for the band gap for temperatures between 400°C to 655°C and including the T^3 dependence for K_i , the temperature dependence turns out to be 0.57 eV which is exactly how expressions 5 and 7 for K_i were arrived at. However, the absolute values of the intrinsic carrier concentrations extrapolated from the expressions of references [31-32] were 4 to 5 times lower than our experimental results needed to be explained. Assuming the temperature dependence of 0.57 eV to be correct, the preexponent (the entropy factor) was adjusted to give the K_i values needed to explain our own experimental results. Considering that the experimental values of n_i exist only for temperatures below 300 K and the expressions of references 31 and 32 when extrapolated from 400° to 655°C give n_i values only 4 to 5 times lower than our experimental results require, the expression for K_i seems to be not too unreasonable. It should be borne in mind however, that the expression for K_i derived from the present work is only valid between 400°C to 655°C . Also, as shown in Figure 13, the temperature dependence of K_i can vary from 0.45 eV to 0.66 eV without adversely affecting our calculations (Figure 12).

Since expression 7 for K_i is only valid for temperatures between $400 - 655^\circ\text{C}$ attempts were made to find an alternative empirical expression for K_i that would yield an intrinsic carrier concentration of $3 \text{ to } 5 \times 10^{16} \text{ cm}^{-3}$, a value experimentally found for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ [3,31,32] at 300 K. Expression for K_i satisfying these criteria is given by:

$$K_i = 7.13 \times 10^{39} \exp (-0.4 \text{ eV}/kT) \text{ cm}^{-6} \quad (9)$$

Expression (9) gives $n_i = 3.7 \times 10^{16} \text{ cm}^{-3}$ at 27°C and the calculated hole concentrations at 77 K based on mass action constants K_i from expression 9

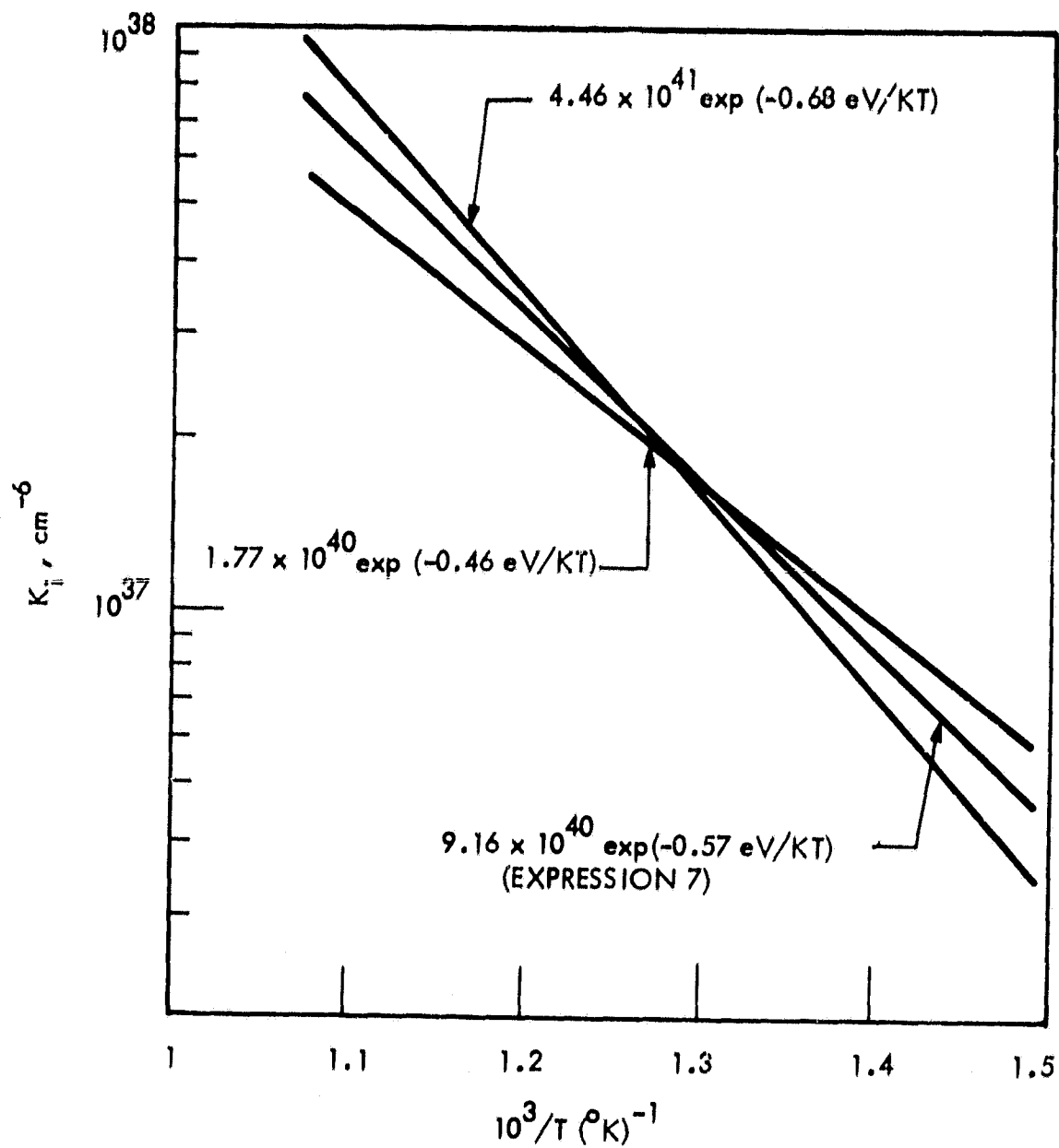
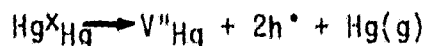


Figure 13: K_i as a function of temperature for $T = 400^\circ\text{C}$ to 655°C from expression (7) of the text; also shown are lines drawn with minimum and maximum slopes corresponding to K_i values differing from those of expression (7) by $\pm 25\%$.

and K''_{VHg} from expression 8 are almost identical to those shown in Figure 2, calculated with mass action constants given by 7 and 8. Table 3 lists the values of K_i for temperatures of 27°C and 400°C - 655°C calculated from both expressions 7 and 9. In situ, high temperature Hall effect measurements are needed to more reliably establish K_i values at high temperatures.

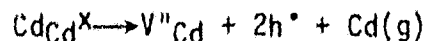
Inspection of Equation 4 indicates that for crystals which are intrinsic at the annealing temperature the second term on the left hand side dominates, with the result that the hole concentration in the cooled crystals is proportional to the value of K_{VHg}/K'' . As a result it is not hard to realize that for given values of K_i the hole concentrations in the cooled crystals depend on K''_{VHg} in just the opposite way as they did with K_i for fixed K''_{VHg} values. Noting from previous arguments that the temperature dependence of K_i can be varied from approximately 0.4 to 0.6 eV without adversely affecting the hole concentrations in the cooled crystals, the accuracy of the enthalpy associated with K''_{VHg} can be estimated to be ± 0.1 eV.

From the present work the enthalpy for the reaction



has been established to be 2.24 eV.

For comparison with CdTe, the enthalpy associated with the reaction



is evaluated to be 4.72 eV [16]. The higher enthalpy associated with a similar defect reaction for CdTe is reasonable in view of the fact that CdTe has a larger melting point and bandgap than $Hg_{0.8}Cd_{0.2}Te$ and, hence, stronger bonding.

Values of some of the mass action constants defined in Table 1 are summarized in Table 4.

The mass action constants K_i and K''_{VHg} established from the present work can explain the results on indium doped [33] as well as phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ [24] satisfactorily.

Table 3

Comparison of values of K_j at various temperatures as calculated from expressions 7 and 9.

Temperature, °C	K_j	
	Expression 7	Expression 9
27	2.45×10^{31}	1.37×10^{33}
400	4.95×10^{36}	7.22×10^{36}
460	1.11×10^{37}	1.27×10^{37}
500	1.77×10^{37}	1.76×10^{37}
550	2.97×10^{37}	2.54×10^{37}
600	4.7×10^{37}	3.5×10^{37}
655	7.37×10^{37}	4.8×10^{37}

Table 4. VALUES OF THE PARAMETERS FOR THE EQUILIBRIUM CONSTANTS
 $K = K_0 \exp (-H/kT)$ DEFINED IN TABLE 1

	Equilibrium Constant	K_0 (site fr., atm)	H(eV)	Source
1.	K_i	4.18×10^{-4}	0.57	This work
2.	$K''VHg$	4.87×10^2	2.24	
3.	$K_{Hg_{0.8}Cd_{0.2}Te}$	2.75×10^9	2.06	Ref. 11
4.	K_{Hg}	7.84×10^4	0.62	} Ref. 9
5.	K_{Te}	1.82×10^5	1.27	

DEFECT ISOTHERMS FOR UNDOPED $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

Once the values of K_i and K''_{VHg} are known, it is possible to calculate the concentrations of various defects as a function of p_{Hg} at any given temperature. Such a defect isotherm for $T = 500^\circ\text{C}$ is shown in Figure 14. As can be seen from the Figure, the crystal is essentially intrinsic except at low Hg pressures at higher temperatures where native acceptor defects begin to become comparable in concentration to intrinsic carriers.

HOLE CONCENTRATION IN UNDOPED $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ UNDER SATURATED AND Te SATURATED CONDITIONS

The highest and the lowest Hg pressures in the experimental data indicated by arrows in Figure 2 correspond to the Hg pressure under Hg saturated conditions and the Hg pressure under Te saturated conditions, respectively [9-11]. Figure 15 shows the hole concentration variation in the cooled crystals as a function of temperature of equilibration for Hg saturated and Te saturated conditions. The temperature dependences of the hole concentration are given by:

$$[h^*] (\text{Hg saturated}) = 1.54 \times 10^{24} \exp (-1.13 \text{ eV}/kT) \text{ cm}^{-3}$$

and

$$[h^*] (\text{Te saturated}) = 2.36 \times 10^{20} \exp (-0.314 \text{ eV}/kT) \text{ cm}^{-3}$$

ISOHOLE CONCENTRATION PLOT FOR $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

Knowledge of K_i and K''_{VHg} permits us to calculate hole concentrations in the cooled crystals as a function of the physicochemical conditions of preparation namely p_{Hg} and T . Such a plot is shown in Figure 16. As can be seen from Figure 16, the undoped material is p-type throughout the existence region for all temperatures as long as the residual foreign acceptor concentration is greater than the residual foreign donor concentration in the crystals. This figure is different from the iso carrier concentration plot reported in references [2,4] where p-type to n-type conversion was attributed to native

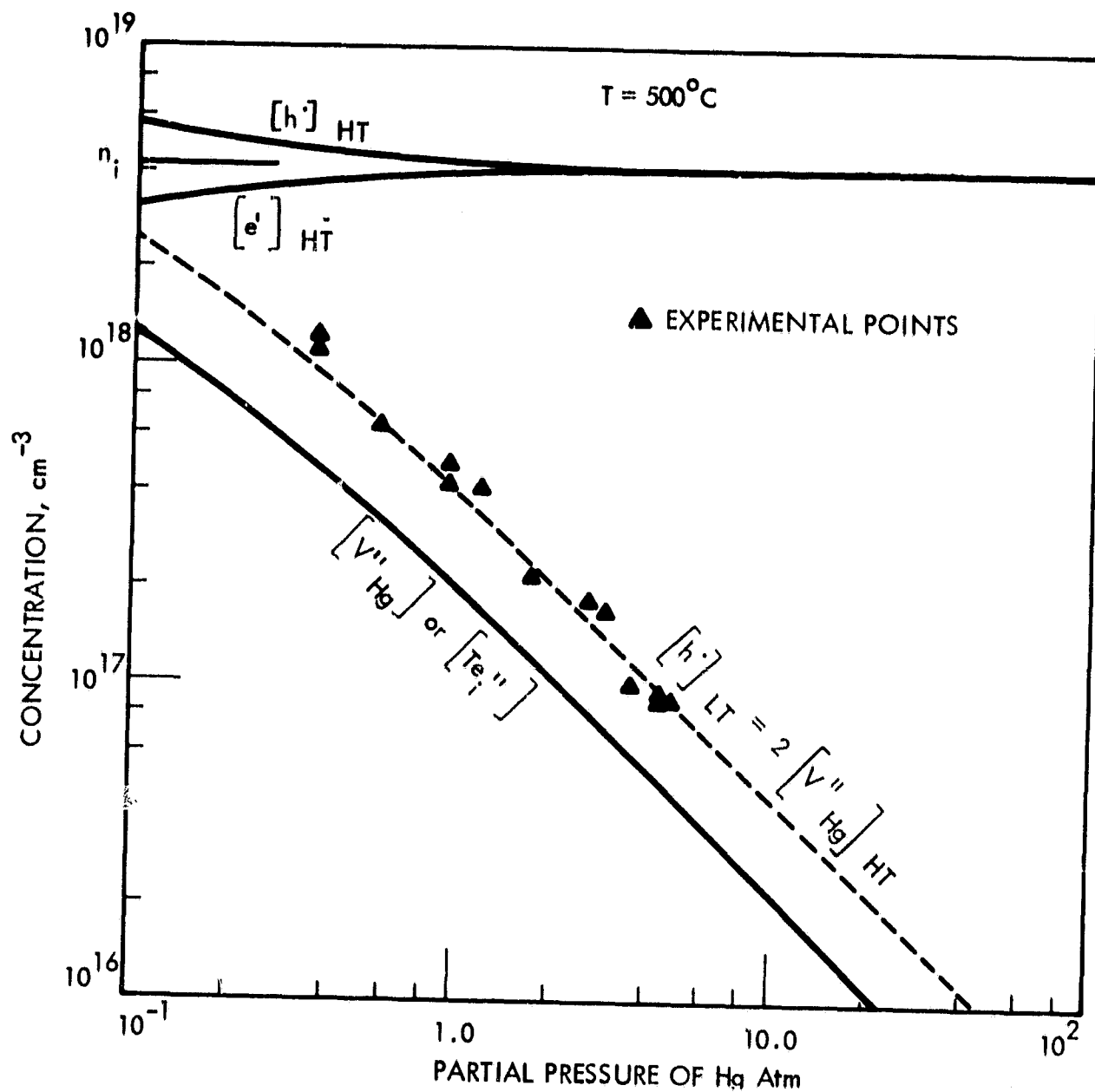


Figure 14: Calculated Defect concentrations as a function of the partial pressure of Hg at the equilibration temperature of 500°C ; dashed line represents the calculated hole concentration in the cooled crystals at 77 K; experimental points are also shown for comparison.

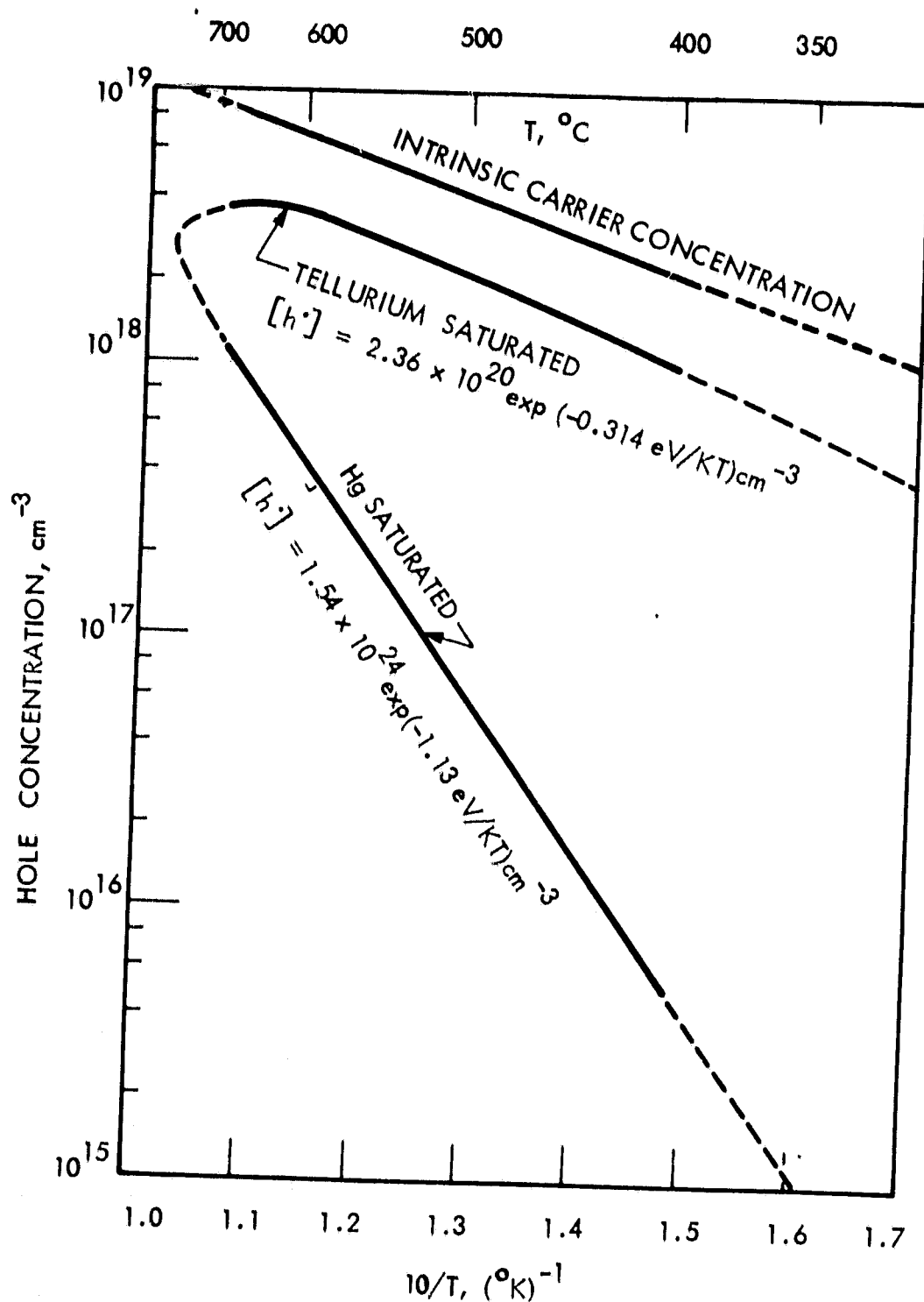


Figure 15: Calculated hole concentration lines at 77 K as a function of temperature for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ equilibrated in Hg saturated and Te saturated conditions and quenched to room temperature. Calculations for temperature ranges outside the experimental work reported in this paper are shown dashed; intrinsic carrier concentration as a function of temperature is also shown.

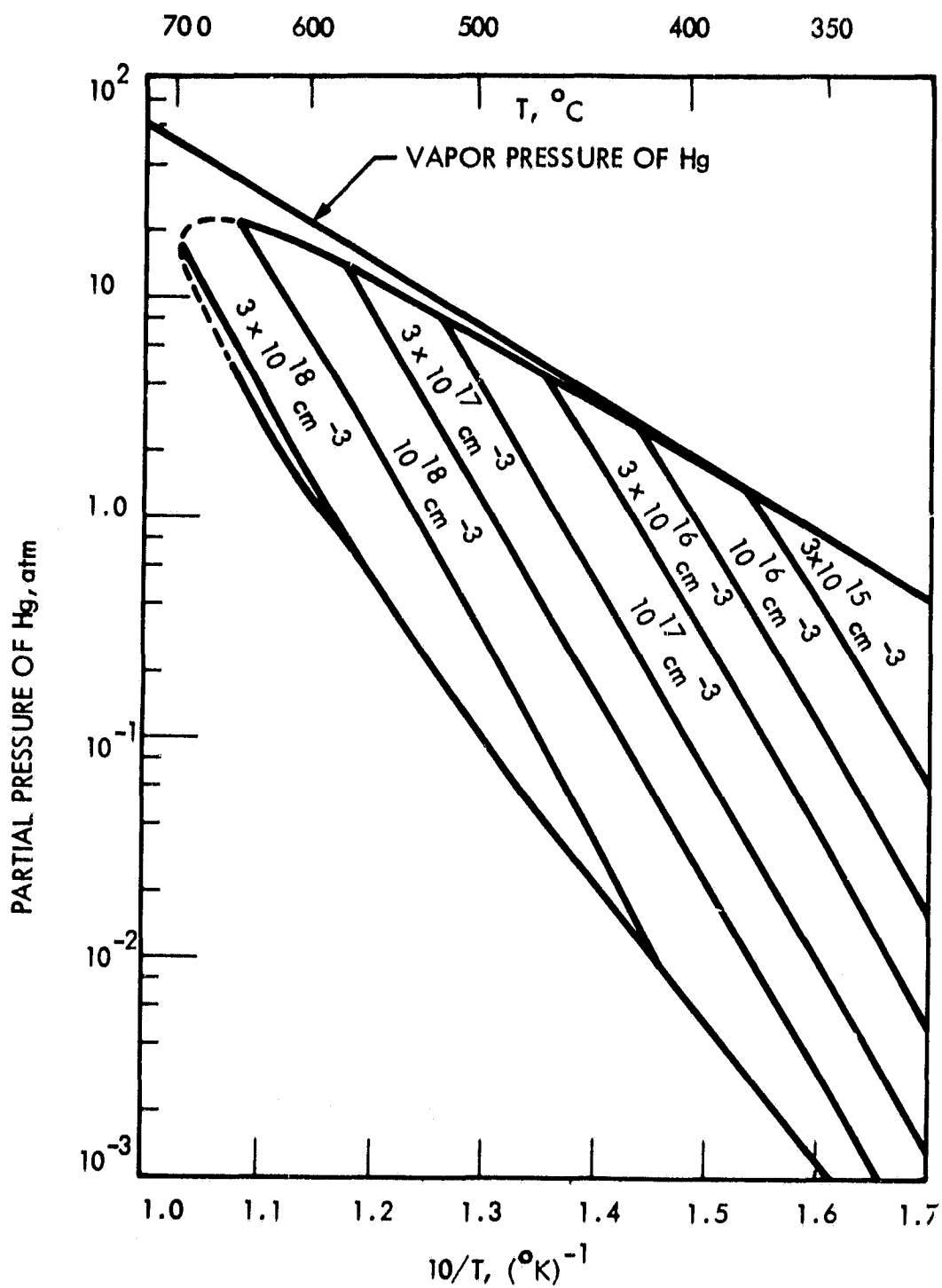


Figure 16: Calculated ISO hole concentration lines at 77 K for Hg_{0.8}Cd_{0.2}Te as a function of the partial pressure of Hg and temperature of equilibration.

donor defects. It can also be seen that the highest deviation from stoichiometry (or the highest hole concentration in the cooled crystals) attainable in undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ is $< 3 \times 10^{18} \text{ cm}^{-3}$.

DEFECT ISOTHERMS FOR COPPER DOPED $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

With the assumption that all of the electrically active copper is present as Cu'_{Hg} , defect concentrations as a function of the electrically active copper concentration and p_{Hg} can be calculated. As before, we shall define high temperature and low temperature states of the crystal using subscripts HT and LT respectively. The complete electroneutrality condition and the copper balance equation are:

$$[e']_{\text{HT}} + 2 [V''_{\text{Hg}}]_{\text{HT}} + [\text{Cu}'_{\text{Hg}}] = [h^*]_{\text{HT}} \quad (9)$$

$$\text{and } [\text{Cu}'_{\text{Hg}}]_{\text{HT}} = [\text{Cu}_{\text{tot}}]_{\text{HT}} \quad (10)$$

In terms of the mass action constants K_i and K''_{VHg} , the electroneutrality condition is rewritten as:

$$(K_i/[h^*])_{\text{HT}} + 2 (K''_{\text{VHg}}/[h^*]^2 p_{\text{Hg}})_{\text{HT}} + [\text{Cu}_{\text{tot}}] = [h^*]_{\text{HT}} \quad (11)$$

or

$$[h^*]_{\text{HT}}^3 - [h^*]_{\text{HT}}^2 [\text{Cu}_{\text{tot}}] - K_i [h^*]_{\text{HT}} = (2 K''_{\text{VHg}}/p_{\text{Hg}})_{\text{HT}} \quad (12)$$

In the cooled crystals, the hole concentration is given by

$$\begin{aligned} [h^*]_{\text{LT}} &= 2[V''_{\text{Hg}}]_{\text{HT}} + [\text{Cu}'_{\text{Hg}}]_{\text{HT}} = \\ &= 2 [V''_{\text{Hg}}]_{\text{HT}} + [\text{Cu}_{\text{tot}}]_{\text{HT}} \end{aligned} \quad (13)$$

or, expressing $[V''_{\text{Hg}}]$ in terms of K''_{VHg} and $[h^*]$, we get:

$$[h^*]_{\text{LT}} = (2 K''_{\text{VHg}}/[h^*]^2 p_{\text{Hg}})_{\text{HT}} + [\text{Cu}_{\text{tot}}]_{\text{HT}} \quad (14)$$

With the knowledge of the mass action constants K_i and K''_{VHg} established for the undoped crystals, defect concentrations ($[\text{V}''\text{Hg}]$, $[\text{h}^+\text{HT}]$, $[\text{h}^+\text{T}]$, etc.) as function of copper concentration for a fixed p_{Hg} or as a function of p_{Hg} for fixed copper concentration can be calculated from equations 12 and 14. Figure 17 shows the defect isotherm for $T = 500^\circ\text{C}$ and $p_{\text{Hg}} = 3$ atm as a function of the total copper concentration in the crystal. Similarity between Figures 10 and 17 is to be noted. While Figure 10 is drawn with approximation to the neutrality condition, Figure 17 has been drawn with the consideration of the complete electroneutrality condition.

IMPERFECT QUENCH FOR HEAVILY COPPER DOPED SAMPLES

The electrically active copper concentration in various samples as inferred from the Hall effect measurements was found to be lower than the total copper concentration in the samples inferred from atomic absorption analysis (Table 5). From arguments in the previous sections, compensation by native donor defects or by copper interstitials (acting as donors) is ruled out to be the explanation. On the other hand, precipitation of copper as neutral copper during quenching or the solubility limit of copper at the equilibration temperatures can explain the discrepancy. If the explanation is one of the solubility limit, it is hard to reason why samples having total copper concentration less than 10^{19} cm^{-3} also show electrically active copper less than the total amount of chemically inferred copper concentrations. Owing to the high diffusivity of Cu in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ [6-7], we are inclined to believe that precipitation of copper as neutral copper during quenching results in the electrically active copper (as found by Hall effect measurements) to be less than that obtained by chemical analysis. The fact that the fraction of electrically active copper decreases for higher and higher copper concentrations (as determined by chemical analysis) also supports the view that precipitation occurs during quenching since the diffusion distance between copper atoms for precipitation to occur can be expected to decrease as $[\text{Cu}_{\text{tot}}]^{-3}$. Efforts to improve the quenching efficiency by breaking open the ampoules and quenching the samples directly in water did not result in any improvement. It appears that the high diffusivity of copper results in an imperfect quench from the equilibration temperatures. If we believe that precipitation occurs during quenching

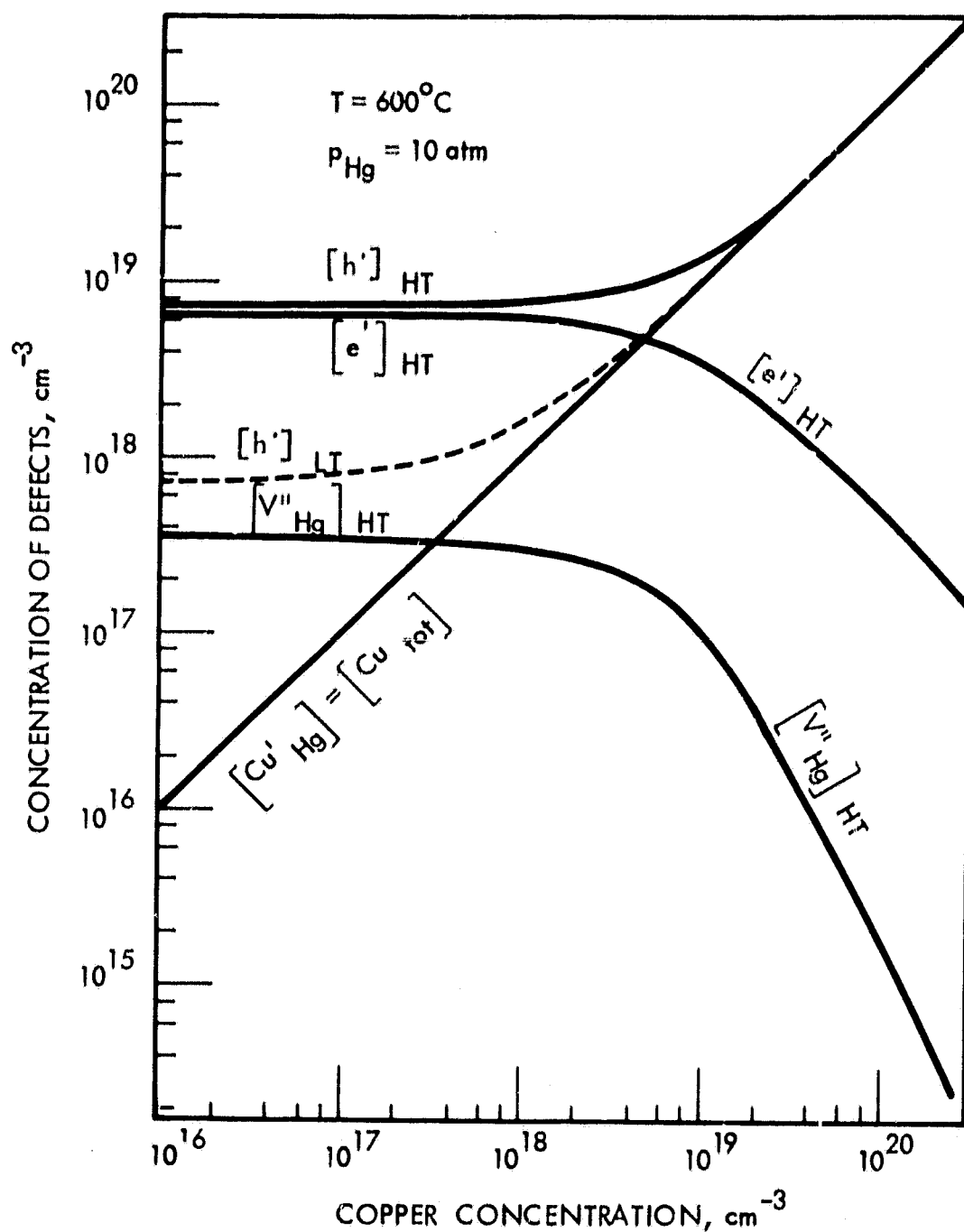


Figure 17: Calculated Defect Concentrations as a function of the electrically active copper concentration in the crystals at the equilibration temperature of 500°C and $p_{\text{Hg}} = 3 \text{ atm}$; dashed line corresponds to the calculated hole concentration in the cooled crystals at 77 K .

Table 5

Comparison of the concentrations of electrically active copper and the total amount of copper (as determined from Atomic Absorption analysis) for samples doped with copper at 500°C and 600°C.

Temperature	Total Copper Concentration, cm^{-3} (Atomic Absorption)	Electrically active copper concentration, cm^{-3} (Hall effect)
500°C	3.4×10^{20}	10^{19}
500°C	1.6×10^{19}	5×10^{18}
500°C	8.7×10^{18}	4.3×10^{18}
600°C	2.2×10^{21}	5×10^{19}
600°C	4.8×10^{20}	1.3×10^{19}
600°C	3×10^{20}	10^{19}
600°C	8.6×10^{18}	4.8×10^{18}

the solubility of electrically active copper at $T = 500 - 600^{\circ}\text{C}$ appears to be in excess of 10^{20} cm^{-3} .

CONCLUSION

Lattice defect models for undoped and copper doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ have been established via Hall effect and mobility measurements on crystals equilibrated under different partial pressures of Hg at high temperatures and quenched to room temperature. According to the models, native donor defects are negligible in concentration, native acceptor defects are doubly ionized and copper acts as a single acceptor occupying Hg lattice sites. Equilibrium constants for the intrinsic excitation constant, as well as the incorporation of the doubly ionized native acceptor defects, have been established.

ACKNOWLEDGEMENT

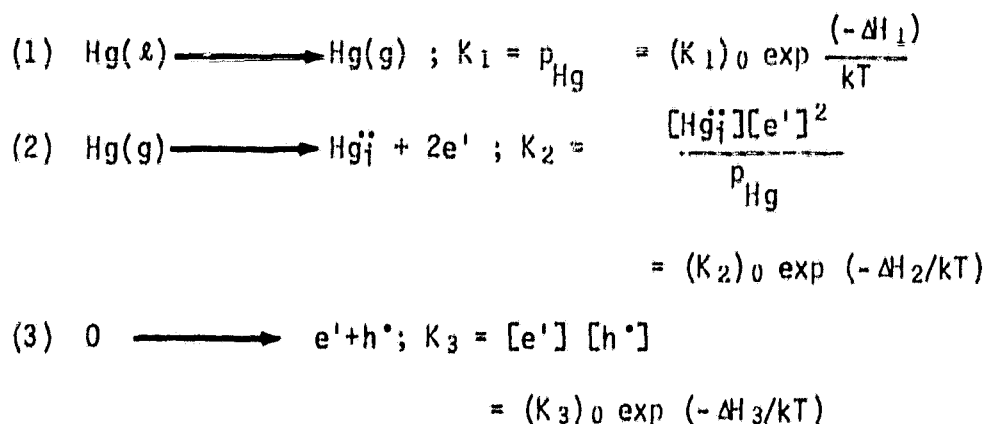
The authors wish to thank J. A. Carruthers of NASA for his interest in this work. Thanks are due to J. L. Schmit for making variable temperature Hall effect measurements for one of the undoped samples. Technical assistance of J. Donovan and P. Crickard with the experimental portion of the work is greatly appreciated. Special thanks are due to R. A. Lancaster for furnishing the crystals.

APPENDIX

TEMPERATURE INDEPENDENCE OF THE NATIVE DONOR DEFECT CONCENTRATION

Results of Reynolds et al [26] on $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ and of Schmit and Stelzer [28] on $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ indicate that the crystals turn n-type below 300-350°C under Hg saturated conditions and the electron concentration under Hg saturated conditions remains independent of the anneal temperature.

If the conversion is thought to be due to some sort of native donor defects, it remains to be explained under what circumstances the temperature independence could arise. For an explanation of this we consider the following reactions:



Two electro neutrality approximations can be considered.

$$(1) \quad [e'] \sim [h^{\bullet}]$$

$$(2) \quad [e'] \sim 2 [\text{Hg}_i^{\bullet\bullet}]$$

$$\text{Case 1: } [e'] = [h^{\bullet}]$$

$$\text{From (2), } [\text{Hg}_i^{\bullet\bullet}] = K_2 p_{\text{Hg}} / [e']^2$$

Substituting $[e'] = [h^\bullet] = K_3$ (from 3) and for p_{Hg} from (1), we get

$$[Hg_i^{\bullet\bullet}] = \frac{K_1 K_2}{K_3} = \frac{(K_1)_0 (K_2)_0}{(K_3)_0} \exp\left(\frac{-\Delta H_1 - \Delta H_2 + \Delta H_3}{kT}\right)$$

If $\Delta H_1 = \Delta H_3 + \Delta H_2$, $[Hg_i^{\bullet\bullet}]$ will be independent of temperature and the electron concentration under Hg saturated conditions will be independent of temperature in the cooled crystals.

$$\text{Case 2: } [e'] \approx 2[Hg_i^{\bullet\bullet}]$$

$$\begin{aligned} \text{From (2), } [Hg_i^{\bullet\bullet}] &= K_2 p_{Hg} / [e']^2 \\ &= K_2 p_{Hg} / 4 [Hg_i^{\bullet\bullet}]^2 \end{aligned}$$

or

$$\begin{aligned} [Hg_i^{\bullet\bullet}] &= (K_2 p_{Hg} / 4)^{1/3} \\ &= \left(\frac{(K_2)_0 (K_1)_0}{4} \right)^{1/3} \exp\left(- \frac{\Delta H_1 - \Delta H_2}{3 kT} \right) \end{aligned}$$

Thus if $\Delta H_1 = -\Delta H_2$, $[Hg_i^{\bullet\bullet}]$ will be independent of temperature and the electron concentration in the cooled crystals under Hg saturated conditions will also be independent of temperature.

It should be noted that while $Hg_i^{\bullet\bullet}$ are considered for the native donor defects here, the arguments are similar if $V_{Te}^{\bullet\bullet}$ are considered instead.

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III.2

Defect chemistry and characterization of Indium doped
 $\text{Hg}_{0.8}\text{Cd}_{0.3}\text{Te}$

LATTICE DEFECTS IN $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ALLOYS†

II DEFECT STRUCTURE OF INDIUM DOPED $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

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Abstract - Hall effect measurements were carried out on indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals quenched to room temperature subsequent to equilibration at 500°C and 600°C under various partial pressures of Hg. All the indium doped crystals were n-type under moderate to high partial pressures of Hg whereas they were p-type at very low Hg pressures. The concentration of electrons obtained in the cooled crystals was lower than the intrinsic carrier concentration at the equilibration temperatures. Also the electron concentration was much lower than the indium concentration in the crystals and was found to increase with increasing Hg pressures at the equilibration temperatures and with increase in the total indium present in the crystals. These inferences have led to a defect model according to which most of the indium is incorporated as In_2Te_3 (S) dissolved in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ (S) with only a small fraction of indium acting as single donors occupying Hg lattice sites. Based on such a model, calculated electron concentrations in the cooled crystals as a function of indium concentration and partial pressure of Hg are in agreement with the experimentally observed values.

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*Electrochemical Society active member

Key words - Defect, Indium doping, $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, electron mobility

INTRODUCTION

The role of indium as a donor and its influence on the native defect structure has been well investigated in CdS [1-2] and CdTe [3-4]. However, such a systematic investigation into the mode of incorporation of indium and its influence on the native defects has not so far been carried out for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys. The defect structure of undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ and the thermodynamic constants for the incorporation of the native acceptor defects and the intrinsic excitation constant in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ have been established in the preceding paper [5] hereafter referred to as Paper I. The present work was undertaken to study the behavior of indium in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ as a function of the physicochemical conditions of preparation (p_{Hg} , T , indium concentration, etc.) and to explain the properties of the indium doped crystals with the knowledge of the defect structure of the undoped crystals[5].

EXPERIMENTAL

Indium was evaporated onto the surface of the undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals ($x = 0.2 \pm 0.005$) and the indium was diffused in at 600°C and $p_{\text{Hg}} = 10$ atm and at 500°C and $p_{\text{Hg}} = 3$ atm. Diffusion times of 24 hours at 600°C and 7 days at 500°C into samples of thickness ≤ 0.004 cm, were found to be adequate for the homogeneous diffusion of indium. The concentration of indium in each sample was determined from atomic absorption analysis carried out by Photometrics, Inc. of Lexington, Massachusetts. The residual impurity concentration in the starting undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ was $\leq 10^{16}$ cm^{-3} . The thicknesses of the samples were minimized as much as possible in order to improve the quenching efficiency from the equilibration temperatures as well as to assure thermodynamic equilibrium within reasonable equilibration times. The equilibration procedure in various Hg atmospheres is similar to what was described in paper I. Subsequent to the equilibration, the samples were quenched to room temperature; in a few cases the samples were air cooled to room temperature from the equilibration temperatures. The samples were lapped, polished and etched in Br-methanol solution. Hall effect and electrical resistivity measurements were made using the van der Pauw method [6]. Magnetic field strengths of 400 Gauss and 4000 Gauss were used for the Hall effect measurements.

RESULTS

As mentioned in paper I, only those Hall effect results which did not vary with the magnetic field and thus showed no mixed type conduction, were used in evaluating the carrier concentrations in the samples using the expression

$$n = \frac{1}{R_H q}$$

The Hall effect data on all the samples doped to reasonable concentrations of indium and annealed at medium to high partial pressures of Hg showed n-type conductivity and the electron concentration in the samples at 77 K and 300 K did not vary much indicating that the indium was all ionized at 77 K. Figures 1 and 2 show the electron concentration in the cooled crystals as a function of the total indium present in the samples at $T = 500^\circ\text{C}$ and 600°C for various partial pressures of Hg. From the figures, it is apparent that the electron concentration in the samples increases with increase in the total indium concentration in the samples and also it increases as the partial pressure of Hg at the equilibration temperatures increases. It is to be noted that although the electron concentration is a function of the total indium present in the crystals, the electron concentration is much lower than the total amount of indium present in the crystals.

Figure 3 shows the electron mobility at 77 K in various indium doped samples as a function of the electron concentration. These mobilities are lower than values reported for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ samples containing low donor concentrations [7].

Figure 4 shows a comparison of the electron concentration obtained at 77 K as a function of the partial pressure of Hg at 500°C for crystals doped with various indium concentrations which were air cooled or quenched to room temperature. It appears from the results that higher electron concentrations are obtained in the air cooled samples than in the quenched samples, the deviations between the two sets of samples being greater at lower Hg pressures.

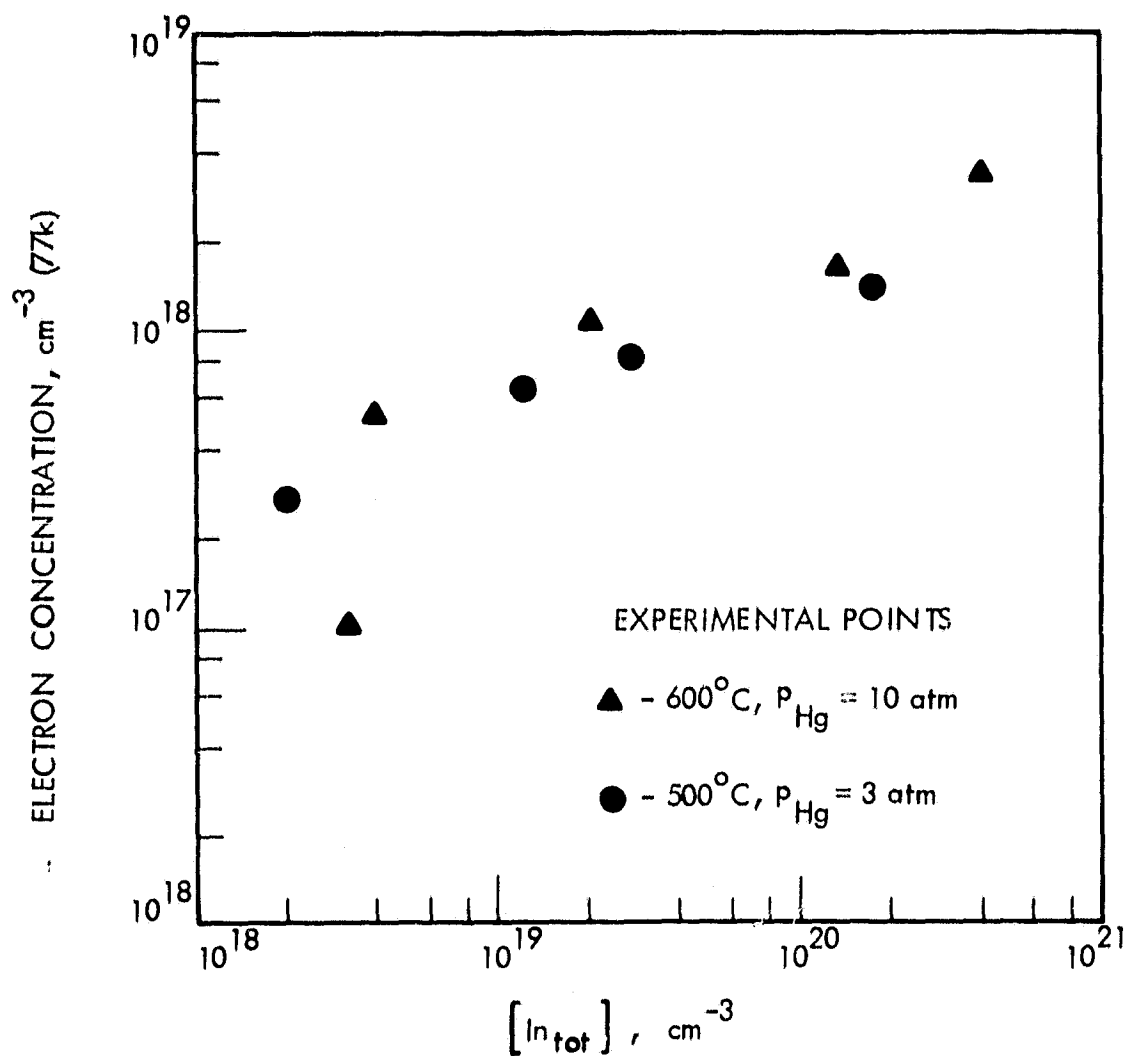


Figure 1: Electron concentration at 77 K as a function of the total indium concentration for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals annealed at 500°C and 600°C under the indicated partial pressures of Hg and quenched to room temperature.

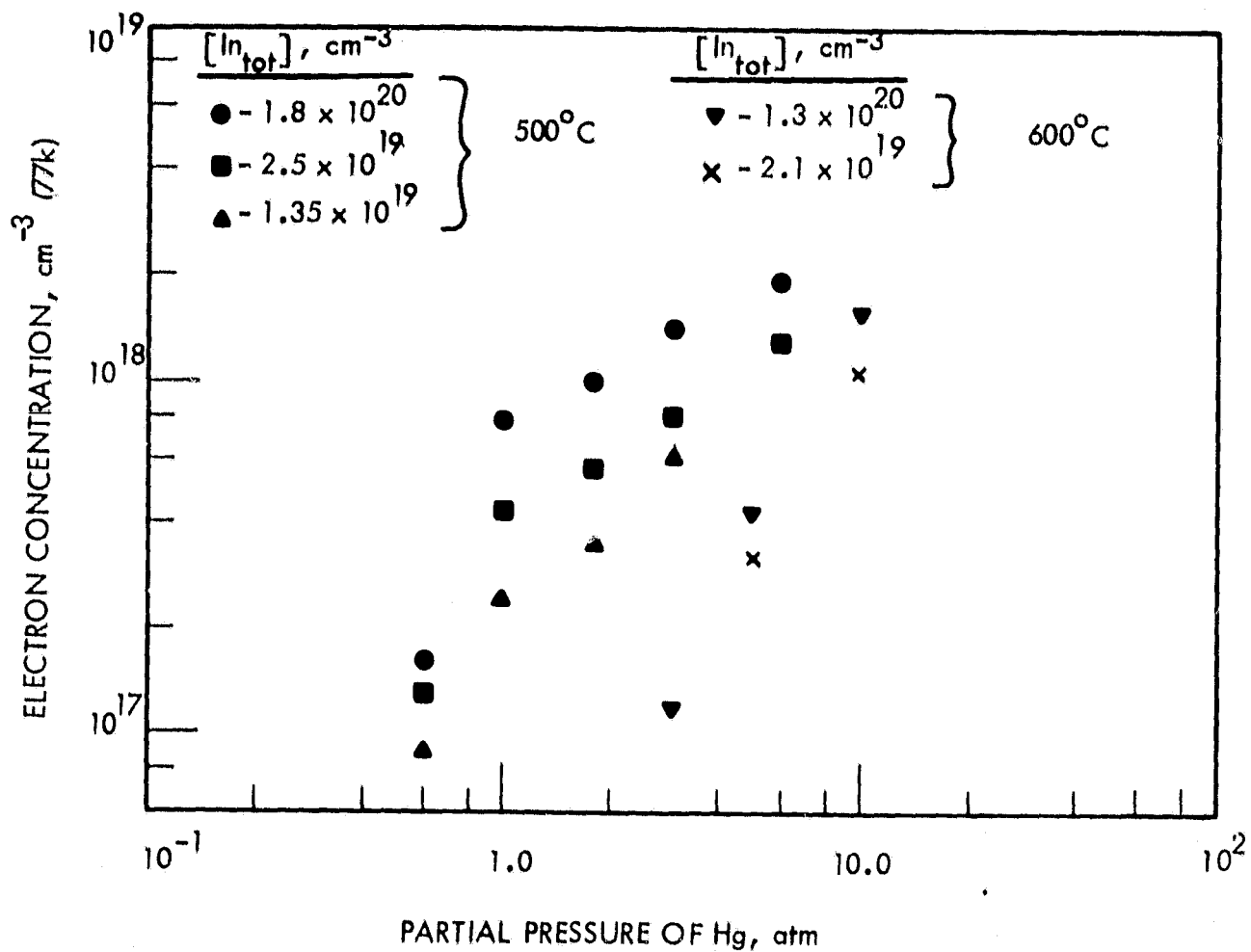


Figure 2: Electron concentration at 77 K as a function of the partial pressure of Hg for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals doped with various amounts of indium and annealed at 500°C and 600°C and quenched to room temperature.

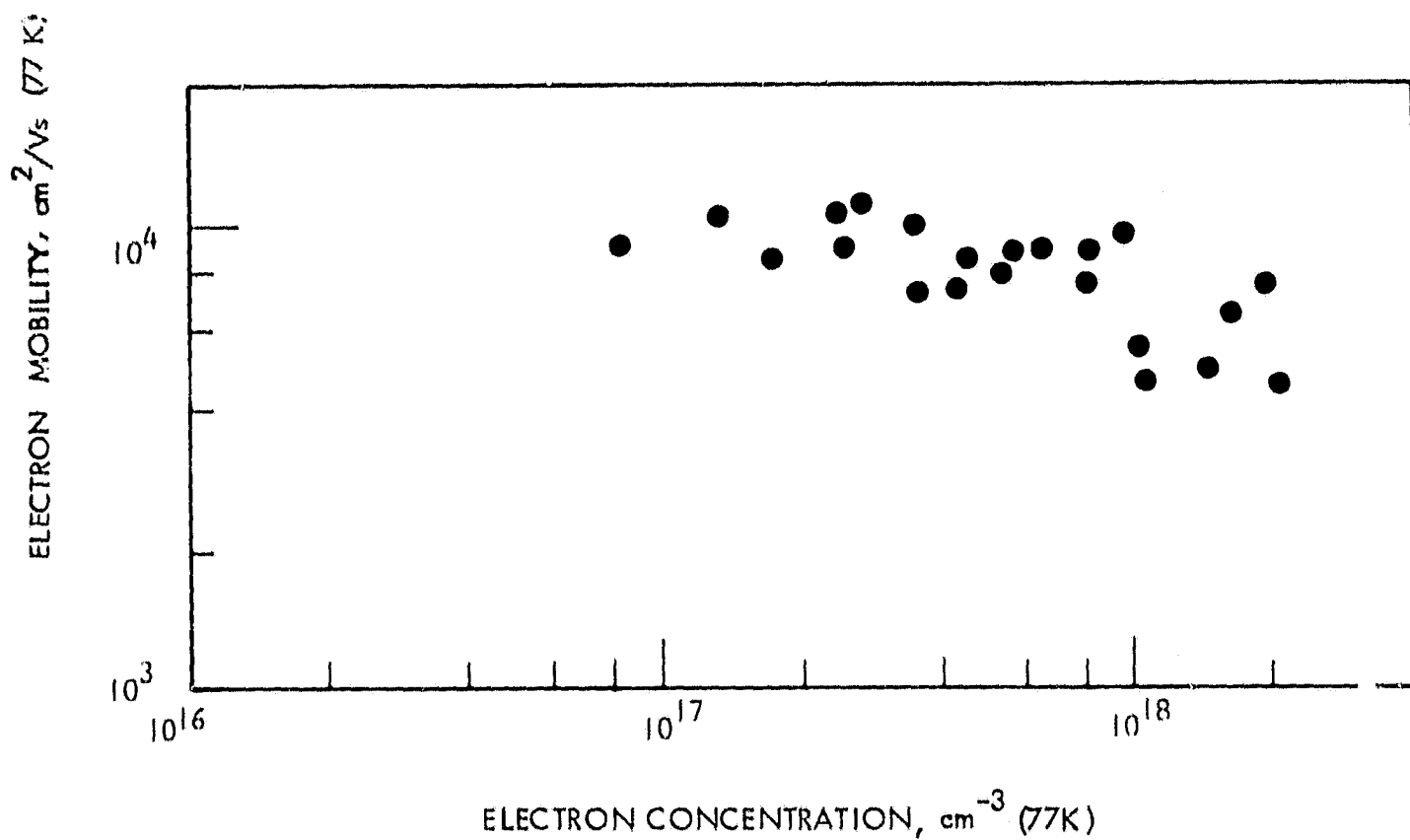


Figure 3: Electron mobility at 77 K as a function of the electron concentration in indium doped Hg_{0.8}Cd_{0.2}Te crystals.

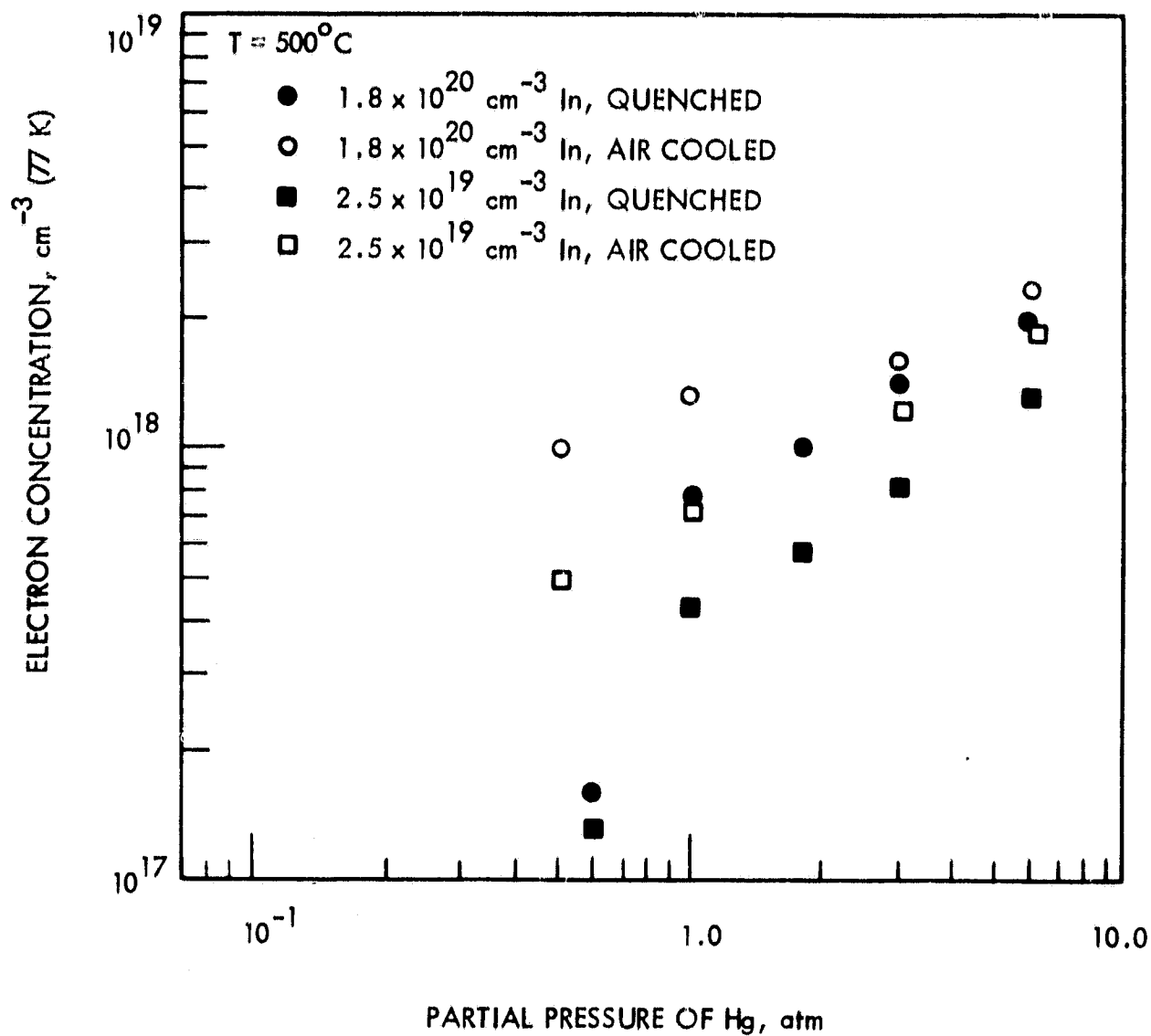


Figure 4: Electron concentration at 77 K as a function of the partial pressure of Hg for crystals doped with different indium concentrations and quenched or air cooled subsequent to equilibration at 500°C.

DISCUSSION

The approach utilized in arriving at a defect model for the indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ is similar to that used for the undoped and copper doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ in paper I. Also any defect model that is established to explain the experimental results in the indium doped crystals should be consistent with the observations in the undoped and the copper doped crystals of paper I.

CHOICE OF A DEFECT MODEL

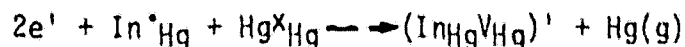
Based on the value of the intrinsic excitation constant K_i arrived at for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ (paper I) for temperatures between 400 - 655°C, data shown in Figures 1 and 2 indicate that the electron concentration obtained in the cooled crystals is much less than the intrinsic carrier concentration at the equilibration temperatures.

Three different models can be considered to explain the electron concentration data shown in Figures 1 and 2.

In the first model considered, a fraction of the indium is assumed to be present as singly positively charged donors occupying Hg lattice sites while the rest of it is assumed to be present as negatively charged associates of singly positively charged indium on Hg lattice sites and doubly negatively charged native acceptor defects. Most of the indium is assumed to be self-compensated as given by the electroneutrality approximation:

$$[\text{In}^+\text{Hg}] = [(\text{InHgV}_{\text{Hg}})'] = [\text{Intot}]/2$$

For such a model the dependence of $[e']$ on $[\text{Intot}]$ and p_{Hg} is inferred from the reaction:



and the mass action constant,

$$K_{(\text{In}_{\text{Hg}}\text{V}_{\text{Hg}})^{\bullet}} = [(\text{In}_{\text{Hg}}\text{V}_{\text{Hg}})^{\bullet}] p_{\text{Hg}} / [e']^2 [\text{In}^{\bullet}_{\text{Hg}}] \quad (1)$$

with,
$$[(\text{In}_{\text{Hg}}\text{V}_{\text{Hg}})^{\bullet}] = [\text{In}^{\bullet}_{\text{Hg}}] = [\text{In}_{\text{tot}}]/2$$

$$[e'] \propto [\text{In}_{\text{tot}}]^0 p_{\text{Hg}}^{1/2} \text{ from (1).}$$

Although this model qualitatively explains the weak donor activity of indium it predicts an independence of electron concentration as a function of the total indium present in the samples, contrary to the results shown in Figures 1 and 2.

In the second model considered, most of the indium is assumed to be present as neutral triplets $(\text{In}_{\text{Hg}}\text{V}_{\text{Hg}}\text{In}_{\text{Hg}})^{\times}$ formed by the association of two singly positively charged indium donor species on Hg lattice sites with a doubly negatively charged native acceptor defect; a small fraction of the indium is assumed to be present unassociated on Hg lattice sites acting as donors.

The reaction of interest is:



and the mass action relation is given by:

$$K_{(\text{In}_{\text{Hg}}\text{V}_{\text{Hg}}\text{In}_{\text{Hg}})^{\times}} = [(\text{In}_{\text{Hg}}\text{V}_{\text{Hg}}\text{In}_{\text{Hg}})^{\times}] p_{\text{Hg}} / [e']^2 [\text{In}^{\bullet}_{\text{Hg}}]^2 \quad (2)$$

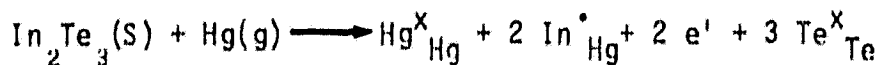
Since we know that the electron concentration obtained in the cooled crystals is less than the intrinsic carrier concentration at the equilibration temperatures, the electroneutrality condition at the equilibration temperatures can be approximated by:

$$[e'] = [h^{\bullet}] = \sqrt{K_i}$$

and for $[(\text{InHgV}_{\text{Hg}}\text{InHg})^{\times}] = [\text{Intot}]/2$ as the approximation to the indium balance equation $[\text{In}^{\bullet}_{\text{Hg}}] \propto [\text{Intot}]^{1/2} p_{\text{Hg}}^{1/2}$ at the equilibration temperatures. Although this model qualitatively explains the variation of electron concentration as a function of the indium in the crystals and the partial pressure of Hg at the equilibration temperatures, the calculated electron concentration in the cooled crystals considering the complete neutrality condition shows a much steeper dependence on p_{Hg} than observed experimentally. Also, the model predicts the crystals to turn p-type even at Hg pressures close to saturation pressures, contrary to the results of Figure 2.

The third model considered is one where most of the indium is assumed to be present as In_2Te_3 dissolved in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$, with a small fraction of In on Hg lattice sites acting as donors. The dependence of the electron concentration on the indium in the crystals and p_{Hg} can be inferred from the reaction describing the incorporation of InHg from the $\text{In}_2\text{Te}_3(\text{S})$ dissolved in $\text{Hg}_{0.2}\text{Cd}_{0.2}\text{Te}$.

The reaction of interest is:



The mass action relation is given by:

$$K_{(\text{In}_2\text{Te}_3 - \text{In}^{\bullet}_{\text{Hg}})} = [\text{In}^{\bullet}_{\text{Hg}}]^2 [\text{e}']^2 / a_{\text{In}_2\text{Te}_3} p_{\text{Hg}} \quad (3)$$

where $a_{\text{In}_2\text{Te}_3}$ is the activity of $\text{In}_2\text{Te}_3(\text{S})$.

$$\text{For } [\text{e}'] = [\text{h}^{\bullet}] = \sqrt{K_i} \gg [\text{In}^{\bullet}_{\text{Hg}}]$$

From (3),

$$[\text{In}^{\bullet}_{\text{Hg}}] \propto a_{\text{In}_2\text{Te}_3}^{1/2} p_{\text{Hg}}^{1/2} \propto \gamma_{\text{In}_2\text{Te}_3}^{1/2} X_{\text{In}_2\text{Te}_3}^{1/2} p_{\text{Hg}}^{1/2} \quad (4)$$

Where $\gamma_{\text{In}_2\text{Te}_3}$ and $X_{\text{In}_2\text{Te}_3}$ stand for the activity coefficient and the mole fraction of $\text{In}_2\text{Te}_3(\text{S})$ dissolved in $(\text{Hg}_{0.8}\text{Cd}_{0.2})\text{Te}(\text{S})$.

In the cooled crystals at 77 K,

$$[e']_{77\text{ K}} [\text{In}^{\bullet}_{\text{Hg}}] \text{ minus } ? [\text{V}^{\bullet\bullet}_{\text{Hg}}] \propto x_{\text{In}_2\text{Te}_3}^{1/2} p_{\text{Hg}}^{1/2} \propto [\text{In}_{\text{tot}}]^{1/2} p_{\text{Hg}}^{1/2} \quad (5)$$

Hence, the dependence of e' in the cooled crystals on the indium concentration in the samples and the partial pressure of Hg at the equilibration temperatures is explainable.

A defect situation where the crystal is saturated with the dopant has been observed for iodine doped CdS [8] where $\text{CdI}_2(\text{s})$ was present as a pure second phase; however, the concentration of the iodine donor species on sulfur lattice sites was independent of the activity of $\text{CdI}_2(\text{s})$, a_{CdI_2} since a_{CdI_2} was taken to be unity for pure $\text{CdI}_2(\text{s})$. In the present case, if the $\text{In}_2\text{Te}_3(\text{s})$ does not dissolve in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}(\text{s})$ but remains as a pure second phase, the activity of $\text{In}_2\text{Te}_3(\text{s})$ becomes unity and the electrically active fraction of indium $[\text{In}^{\bullet}_{\text{Hg}}]$ becomes independent of the activity of In_2Te_3 and in turn becomes independent of the amount of $\text{In}_2\text{Te}_3(\text{s})$ or the total amount of indium present in the crystals (equations 3 to 5) contrary to our experimental observations (Figures 1 and 2). However, if $\text{In}_2\text{Te}_3(\text{s})$ dissolves in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}(\text{s})$, the activity of $\text{In}_2\text{Te}_3(\text{s})$, $a_{\text{In}_2\text{Te}_3}$ becomes a variable, increasing with increasing amount of the dissolved $\text{In}_2\text{Te}_3(\text{s})$ and reaching a value of unity when the solubility limit is reached and $\text{In}_2\text{Te}_3(\text{s})$ becomes a pure second phase. For such a situation, the electrically active fraction of Indium $[\text{In}^{\bullet}_{\text{Hg}}]$ becomes a function of the activity of $\text{In}_2\text{Te}_3(\text{s})$ and thereby a function of the amount of $\text{In}_2\text{Te}_3(\text{s})$ or the total amount of indium present in the crystals (Equations 3 to 5); the electron concentration in the cooled crystals which is directly proportional to the amount of the electrically active indium becomes a function of the total indium present in the crystals (Expression 5). Hence the dissolution of $\text{In}_2\text{Te}_3(\text{s})$ in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}(\text{s})$ is an essential requirement to explain the dependence of the electron concentration in the cooled crystals on the total indium present in the crystals. It should also be mentioned at this stage that if indium in interstitial sites is considered to be the donor species instead of indium on Hg lattice sites the incorporation reaction is written as:

$\text{In}_2\text{Te}_3(\text{s}) + 3 \text{Hg}(\text{g}) \rightarrow 2 \text{In}_i^\bullet + 2 \text{e}' + 3 \text{Hg}_{\text{Hg}}^{\text{x}} + 3 \text{Te}_{\text{Te}}^{\text{x}}$ and the mass action constant $K = \frac{[\text{In}_i^\bullet]^2 [\text{e}']^2}{a_{\text{In}_2\text{Te}_3} p_{\text{Hg}}^3}$; for an intrinsic crystal with $[\text{e}'] = [\text{h}^\bullet] = \sqrt{k_i}$,

$$[\text{In}_i^\bullet] \propto p_{\text{Hg}}^{3/2} a_{\text{In}_2\text{Te}_3}^{1/2}$$

The electron concentration in the cooled crystals for such a situation can be expected to be dependent on p_{Hg} much stronger than experimentally observed. Also, such a model predicts that the crystals turn p-type at Hg pressures close to saturation pressures contrary to the experimental results (Figures 1 and 2). Thus, in addition to the requirement that $\text{In}_2\text{Te}_3(\text{s})$ be in solid solution of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}(\text{s})$ the requirement that the majority of the electrically active indium be present substitutionally on Hg lattice sites rather than in interstitial sites must also be satisfied in order to explain the experimental results.

The fact that the experimental results require that In_2Te_3 be in solution of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ up to about 1 to 2 mol percent is not unreasonable. HgTe , CdTe , and In_2Te_3 all have zinc blende structures with not too largely different lattice parameters (6.43 \AA for HgTe , 6.47 \AA for CdTe and 6.15 \AA for In_2Te_3) and, in fact, it has been established by Woolley et al [9] and Spencer [10] that amounts of up to 15 mol percent In_2Te_3 dissolve in HgTe and the energy gap increases with increasing In_2Te_3 concentration somewhat significantly beyond about 5 mol percent. We, however, assume that in our experiments, for In_2Te_3 concentration less than 1 mol percent the influence on the energy gap of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ is negligible. The assumption appears justifiable since no drastic variation in the concentration of carriers is encountered with increasing indium concentration in the crystal. Pure In_2Te_3 is known to be p-type with an energy gap of 0.3 eV [10] and in fact one of the samples that was doped to 5×10^{21} atoms/c.c. of indium showed excessive In_2Te_3 formation and the sample was p-type.

Preliminary x-ray and Auger analysis data also seem to support the model of indium being present as $\text{In}_2\text{Te}_3(\text{s})$ dissolved in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}(\text{s})$. Auger analysis of the surface of a sample containing greater than 10^{21} cm^{-3} of

indium indicated the surface to be rich in indium and tellurium and the composition corresponded to In_2Te_3 . X-ray analyses indicated evidence of lattice parameter changes with an increase in the concentration of indium from $3 \times 10^{19}\text{cm}^{-3}$ to $3 \times 10^{20}\text{cm}^{-3}$ with no evidence of the presence of a second phase whereas clear evidence of the presence of a second phase was obtained in samples containing greater than 10^{21}cm^{-3} of indium. Although not entirely conclusive, these data seem to support the idea that $\text{In}_2\text{Te}_3(\text{s})$ is soluble in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ from one to five mole percent at $500^\circ\text{C} - 600^\circ\text{C}$.

ANALYSIS OF THE CARRIER CONCENTRATION IN THE COOLED CRYSTALS

Denoting the high temperature defect state by subscript HT, the complete electroneutrality condition and the indium balance equation can be written as:

$$[e']_{\text{HT}} + 2 [V''_{\text{Hg}}]_{\text{HT}} = [\text{In}^\bullet_{\text{Hg}}]_{\text{HT}} + [h^\bullet]_{\text{HT}} \quad (6)$$

and

$$[\text{In}^\bullet_{\text{Hg}}]_{\text{HT}} + 2 [\text{In}_2\text{Te}_3]_{\text{HT}} = [\text{In}_{\text{tot}}] \quad (7)$$

Expressing all the quantities in the electroneutrality condition (6) in terms of the mass action constants defined in paper I, we get:

$$[e']_{\text{HT}} + 2 K''_{\text{VHg}} [e']_{\text{HT}}^2 / K_i^2 p_{\text{Hg}} = [\text{In}^\bullet_{\text{Hg}}] + K_i / [e']_{\text{HT}}$$

or

$$2 [e']_{\text{HT}}^3 K''_{\text{VHg}} / K_i^2 p_{\text{Hg}} + [e']_{\text{HT}}^2 - [\text{In}^\bullet_{\text{Hg}}] [e']_{\text{HT}} - K_i = 0 \quad (8)$$

Owing to the narrow bandgap of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$, the correctness of the assumption of $K_i = [e'] [h^\bullet] = \text{constant}$ for a fixed temperature for large donor or acceptor concentrations is arguable. Since all our experimental results have shown systematic variations of carrier concentrations as a function of the imposed physicochemical conditions in accordance with the mass action approach, we feel our assumption is a valid one.

In the crystals quenched to room temperature from the equilibration temperatures,

$$[e']_{77 K} = [In^{\bullet}_{Hg}]_{HT} \text{ minus } 2 [V''_{Hg}]_{HT}$$

or

$$[e']_{77 K} = [In^{\bullet}_{Hg}] - 2 K''_{VHg} [e']^2_{HT} / K_i^2 P_{Hg} \quad (9)$$

values of the mass action constants K_i and K''_{VHg} are given by (paper I):

$$K_i = 9.16 \times 10^{40} \exp (-0.57 \text{ eV/KT}) \text{ cm}^{-6} \quad (10)$$

and

$$K''_{VHg} = 1.58 \times 10^{69} \exp (-2.24 \text{ eV/KT}) \text{ cm}^{-9} \text{ atm} \quad (11)$$

with the knowledge K''_{VHg} and K_i Equation 8 gives $[e']_{HT}$ and $[V''_{Hg}]$ as a function of $[In^{\bullet}_{Hg}]$ for various partial pressures of Hg.

The product of the mass action constant defined by Equation 3 and the activity of $In_2Te_3(s)$, $K(In_2Te_3-In^{\bullet}_{Hg}) a_{In_2Te_3}$ and $[e']_{77K}$ are also immediately obtained as a function of $[In^{\bullet}_{Hg}]$ from Equations (3) and (9) respectively. Comparison of the calculated $[e']_{77 K}$ as a function of $[In^{\bullet}_{Hg}]$ with the experimental values of Figure 1 gives the concentration of the electrically active fraction of indium as a function of the total indium present in the crystals as shown in Figure 5. Values of $K(In_2Te_3-In^{\bullet}_{Hg}) \cdot a_{In_2Te_3}$ calculated earlier as a function of $[In^{\bullet}_{Hg}]$ can then be related to the total indium concentration in the crystals and in turn to the amount of In_2Te_3 present in the crystals from the indium balance Equation 6. Figure 6 shows $K(In_2Te_3-In^{\bullet}_{Hg}) a_{In_2Te_3}$ as a function of $[In_2Te_3]$ present in the crystals. Since the slope of the curves on the log-log scale is different from unity, it appears that the activity coefficient of $In_2Te_3(S)$ dissolved in $Hg_{0.8}Cd_{0.2}Te(S)$ is not constant, but varies with the amount of $In_2Te_3(S)$. Once the values of $K(In_2Te_3 - In^{\bullet}_{Hg}) a_{In_2Te_3}$ as a function of $In_2Te_3(S)$ are known from Figure 6, it is possible to calculate $[e']_{77K}$, $[e']_{HT}$, $[V''_{Hg}]_{HT}$, $[In^{\bullet}_{Hg}]$, and $[In_2Te_3]$ as a function of $[In_{tot}]$ and P_{Hg} from Equations (3), (7), (8), and (9).

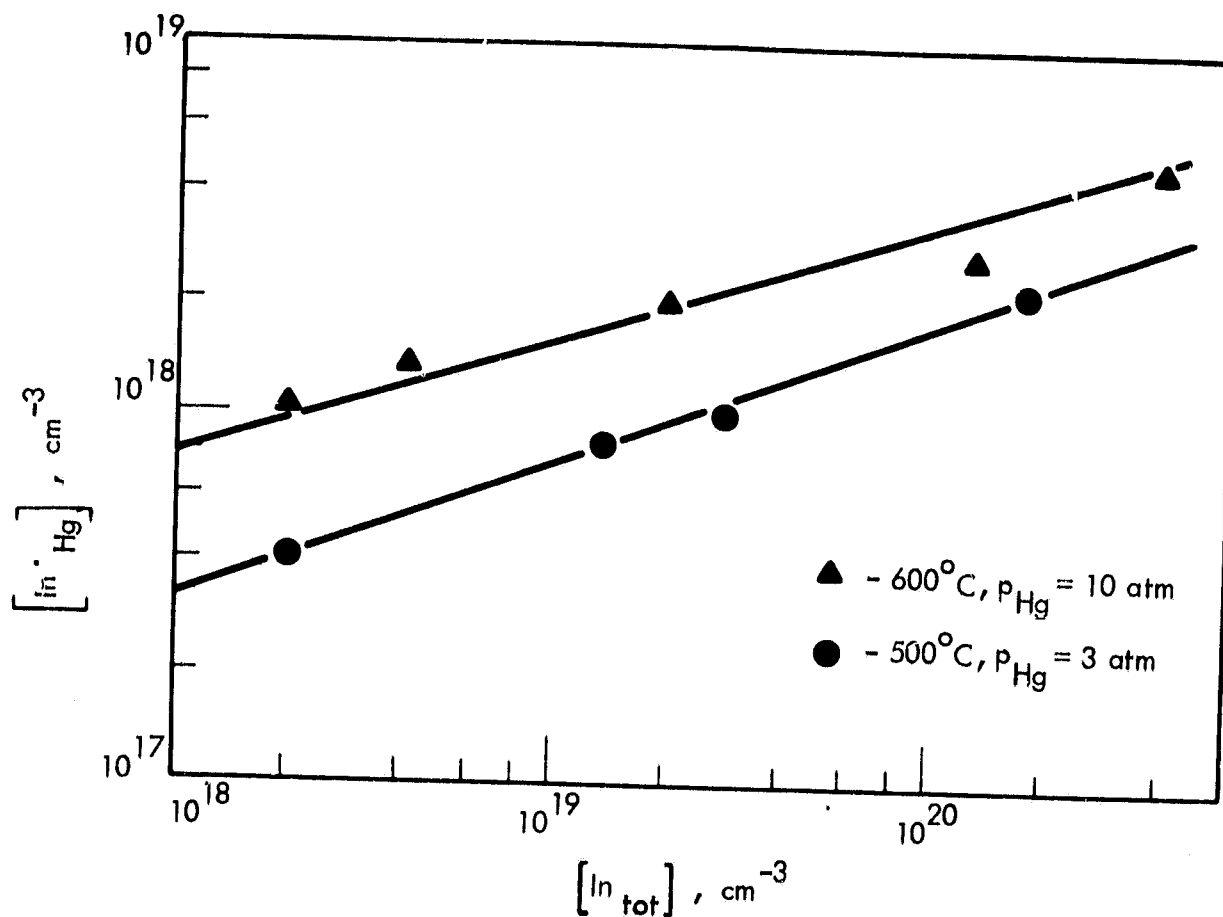


Figure 5: Concentration of electrically active indium as a function of the total indium present in the crystals subsequent to equilibration at 500°C, $p_{Hg} = 3$ atm and at 600°C, $p_{Hg} = 10$ atm.

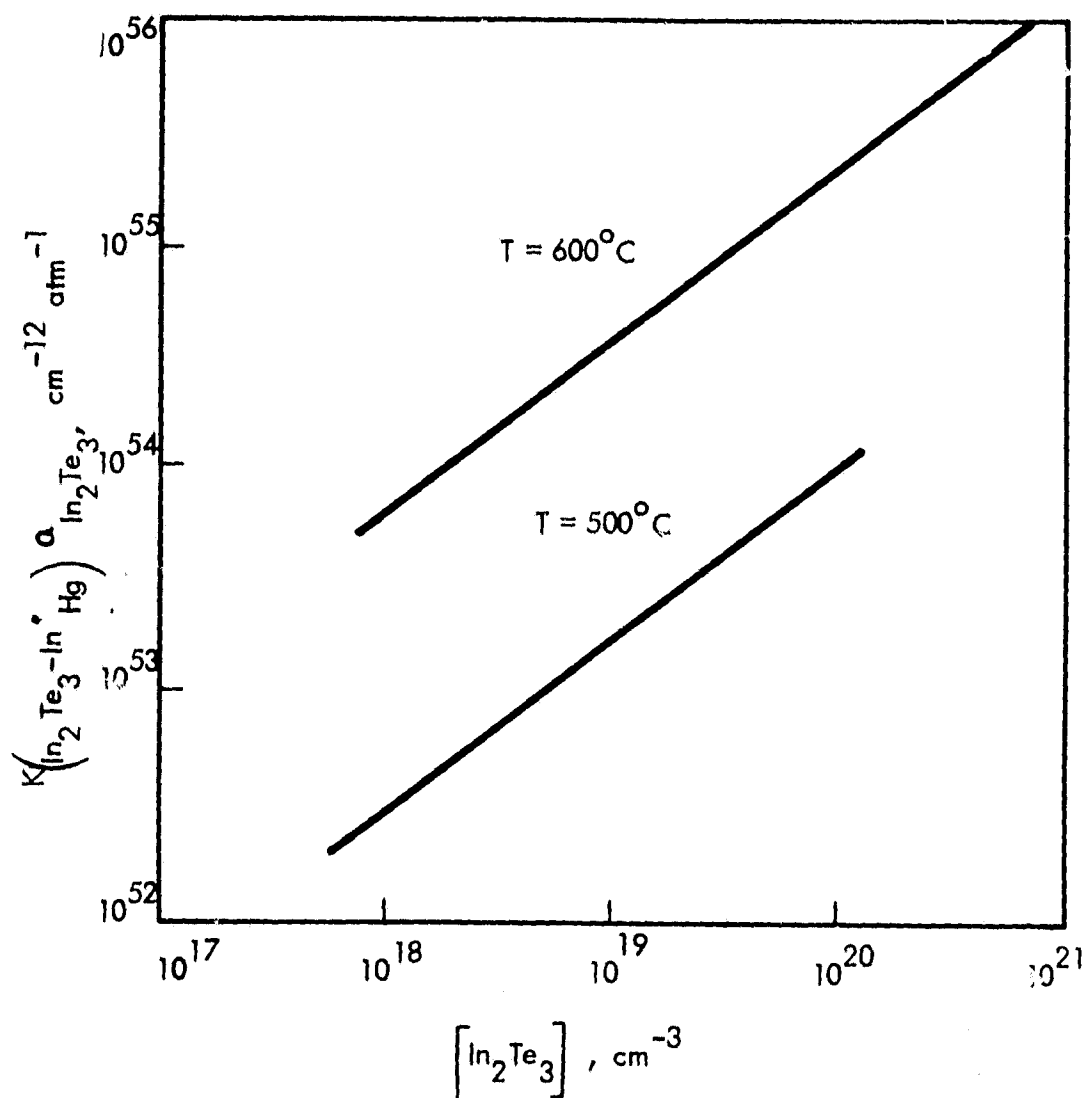


Figure 6: Calculated value of the product of the mass action constant $K(\text{In}_2\text{Te}_3 - \text{In}^*\text{Hg})$ and the activity of $\text{In}_2\text{Te}_3 (\text{S})$ in solution of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te} (\text{S})$ ($= [\text{In}^*\text{Hg}]^2[\text{e}']^2/p_{\text{Hg}}$; expression (3) in the text) as a function of the concentration of In_2Te_3 present in the indium doped crystals subsequent to equilibration at 500°C and 600°C .

Figures 7 and 8 show the calculated defect concentrations at $T = 500^{\circ}\text{C}$, $p_{\text{Hg}} = 3 \text{ atm}$, and $T = 600^{\circ}\text{C}$, $p_{\text{Hg}} = 10 \text{ atm}$ as a function of the indium concentration in the crystals. Calculated values of the carrier concentrations in the cooled crystals are also shown along with the experimental values. The agreement between the calculated values and the experimental ones appears satisfactory. The figures also predict that the crystal is essentially intrinsic with most of the indium being present as In_2Te_3 with only a small fraction present as single donors occupying Hg lattice sites. The concentration of the native acceptor defects is essentially constant in the figures since the partial pressure of Hg is kept constant and the crystals are essentially intrinsic.

Figure 9 shows the calculated defect concentrations at $T = 500^{\circ}\text{C}$ as a function of the partial pressure of Hg for a fixed indium concentration in the crystal. It can be noticed from the figure that although the total indium concentration is fixed in the crystal, the amount of the electrically active indium varies as a function of the partial pressure of Hg as predicted from the incorporation reaction for In_{Hg} from $\text{In}_2\text{Te}_3(\text{S})$ (Equation 3). The concentration of the native acceptor defects ($[\text{V}''_{\text{Hg}}]$) also varies in Figure 9 since the partial pressure of Hg is a variable. The calculated electron concentration values at 77 K as a function of p_{Hg} are in agreement with the experimental values shown in the figure. The p to n transition in the cooled crystals (Figures 7 through 9) occurs when $[\text{In}^{\bullet}_{\text{Hg}}] = 2 [\text{V}''_{\text{Hg}}]$.

Figures 10 and 11 show the calculated electron concentrations at 77 K for various indium concentrations in the crystals at $T = 500^{\circ}\text{C}$ and 600°C as a function of p_{Hg} . Agreement between the calculated values and the experimental ones appears satisfactory.

It is interesting to note from figures 8 through 11 that even for very high indium concentrations the crystals turn p-type under low Hg pressures thus demonstrating the complexity of dopant incorporation in defect semiconductors.

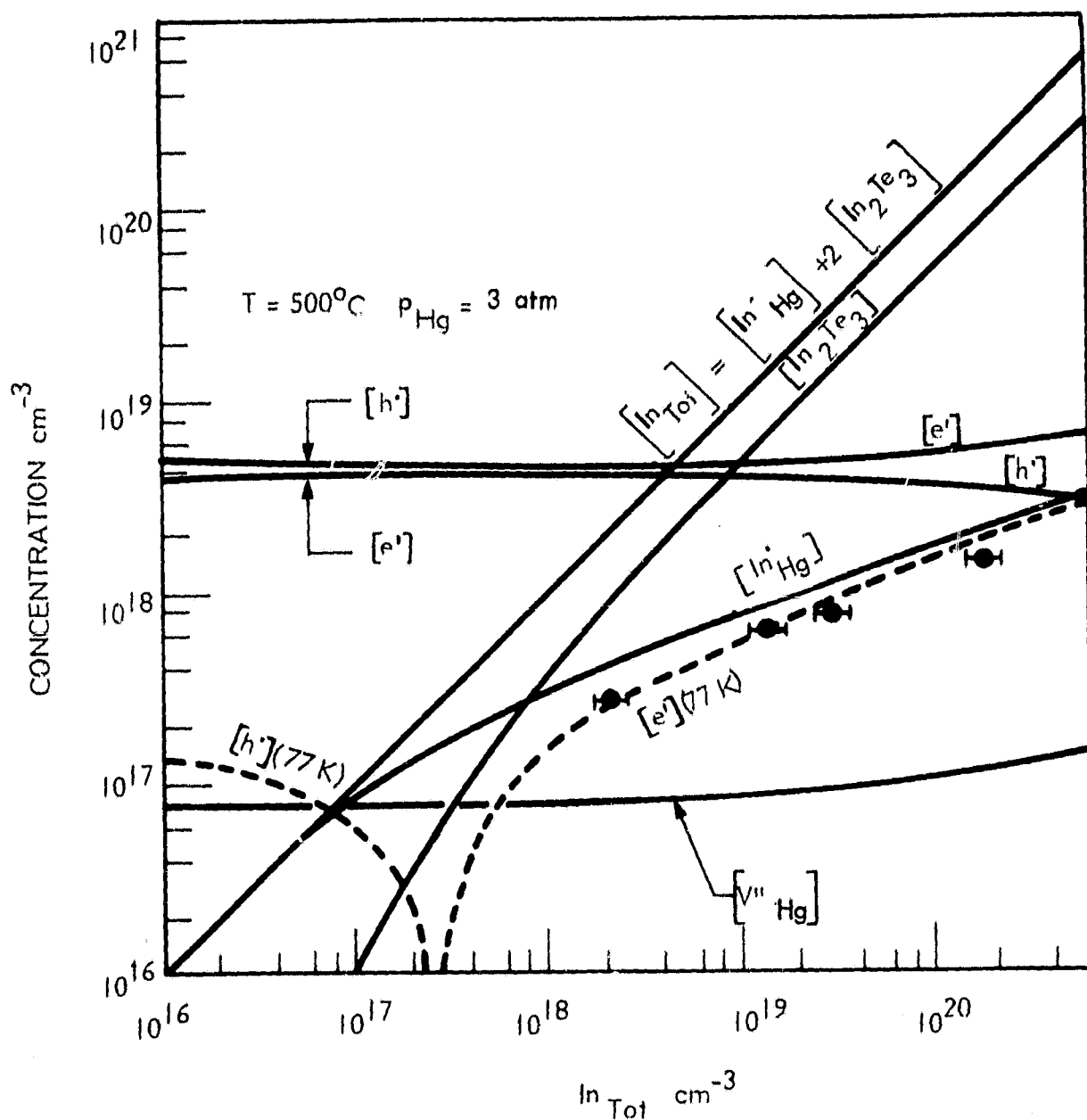


Figure 7: Calculated defect concentrations ($[\text{e}^{\bullet}]$, $[\text{h}^{\bullet}]$, $[\text{V}''\text{Hg}]$, $[\text{In}^{\bullet}\text{Hg}]$ and $[\text{In}_2\text{Te}_3]$) as a function of the total indium present in the indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals subsequent to equilibration at 500°C and $p_{\text{Hg}} = 3 \text{ atm}$; dashed lines show the calculated carrier concentrations obtained in the cooled crystals at 77 K; experimental points are also shown for comparison.

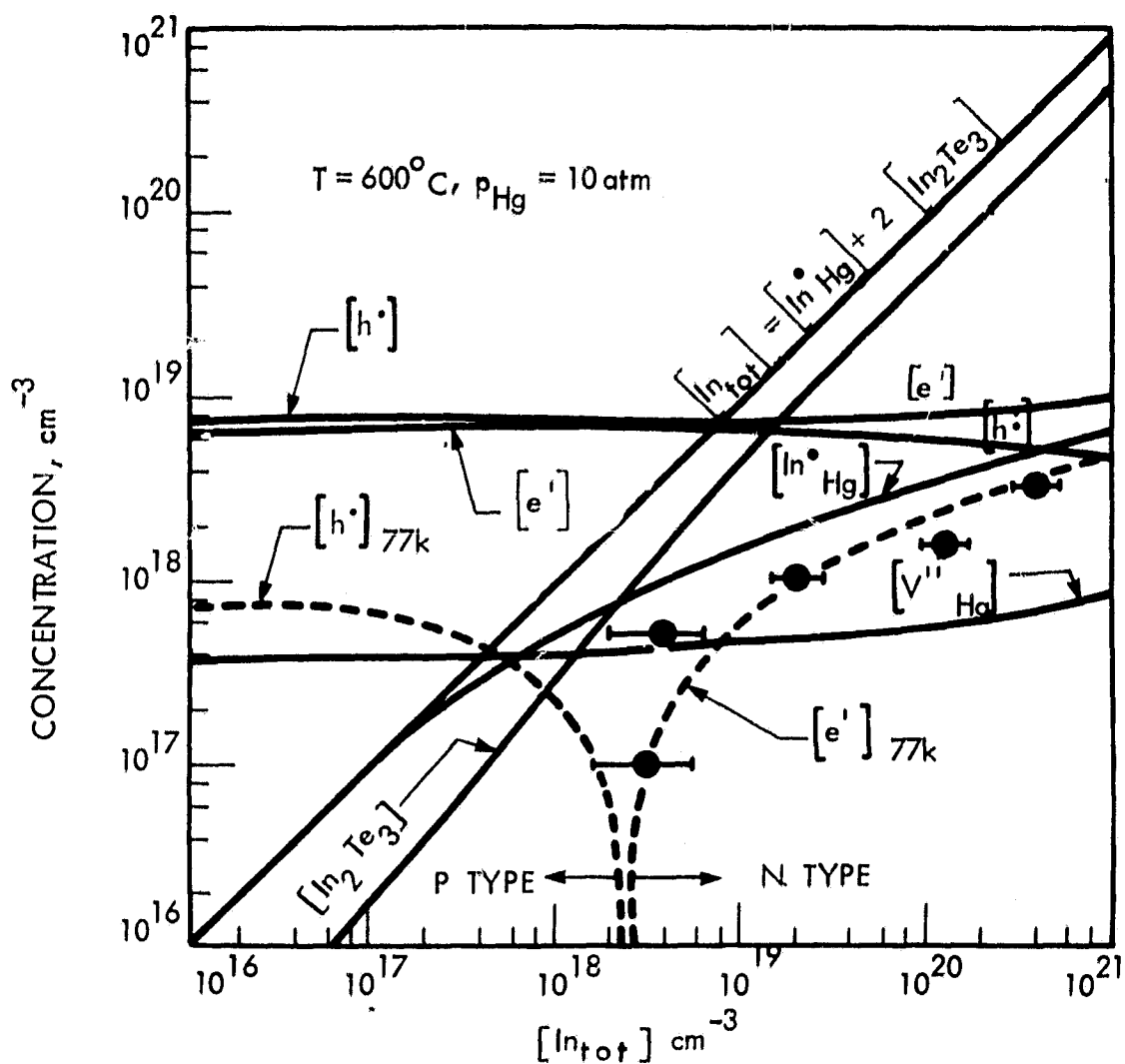


Figure 8: Calculated defect concentrations ($[e']$, $[h\cdot]$, $[V''_{Hg}]$, $[In\cdot_{Hg}]$ and $[In_2Te_3]$) as a function of the total indium present in the indium doped $Hg_{0.8}Cd_{0.2}Te$ crystals subsequent to equilibration at $600^\circ C$ and $p_{Hg} = 10 \text{ atm}$; dashed lines show the calculated carrier concentrations obtained in the cooled crystals at 77 K; experimental points are also shown for comparison.

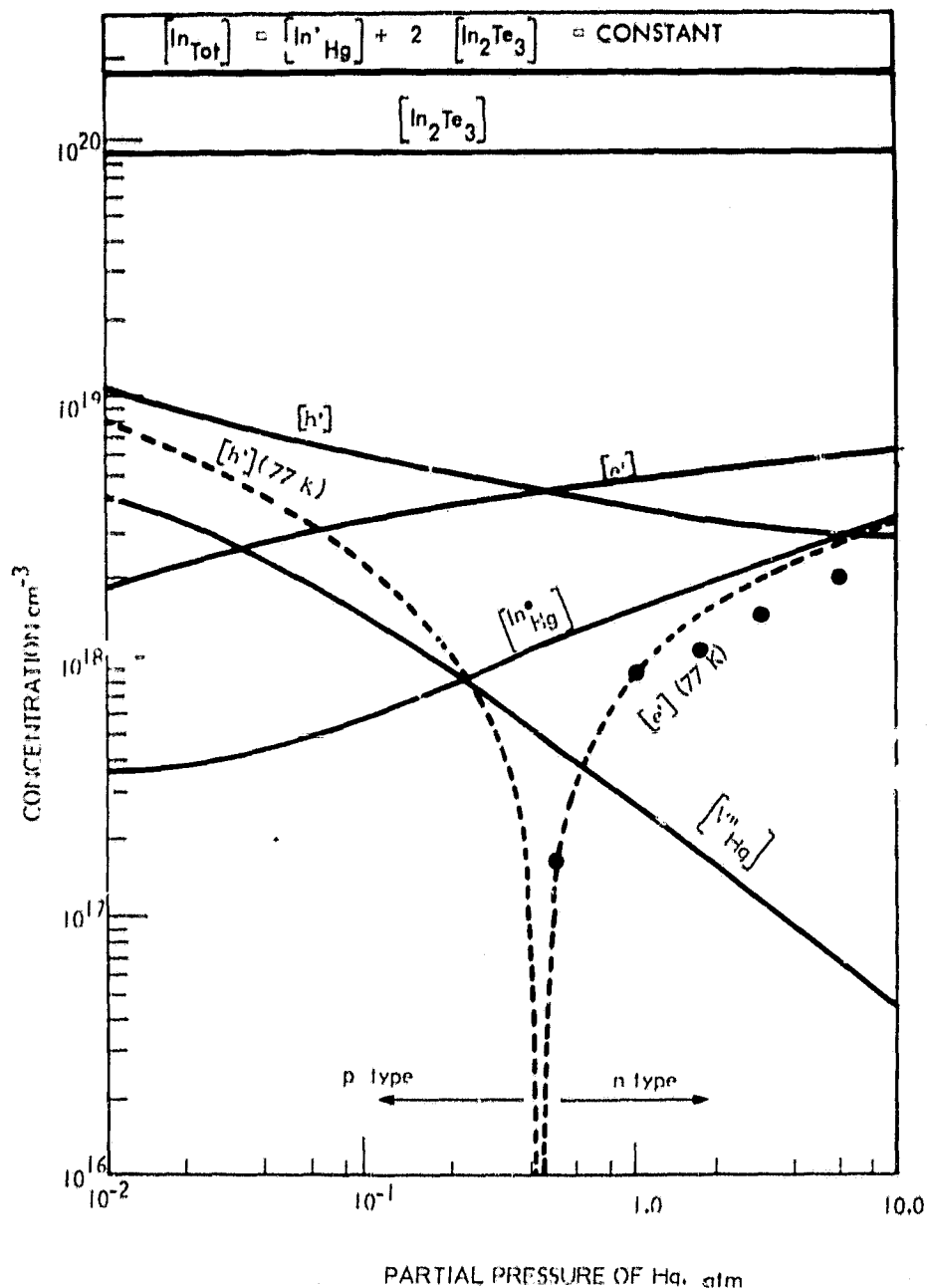


Figure 9: Calculated defect concentrations ($[e']$, $[h^{\bullet}]$, $[V''Hg]$, $[In^{\bullet}Hg]$ and $[In_2Te_3]$) as a function of the partial pressure of Hg at the equilibration temperature of 500°C for a fixed indium concentration of $1.8 \times 10^{20} \text{ cm}^{-3}$ in $Hg_{0.8}Cd_{0.2}Te$ crystals; dashed lines show the calculated carrier concentrations obtained in the cooled crystals at 77 K; experimental points are also shown for comparison.

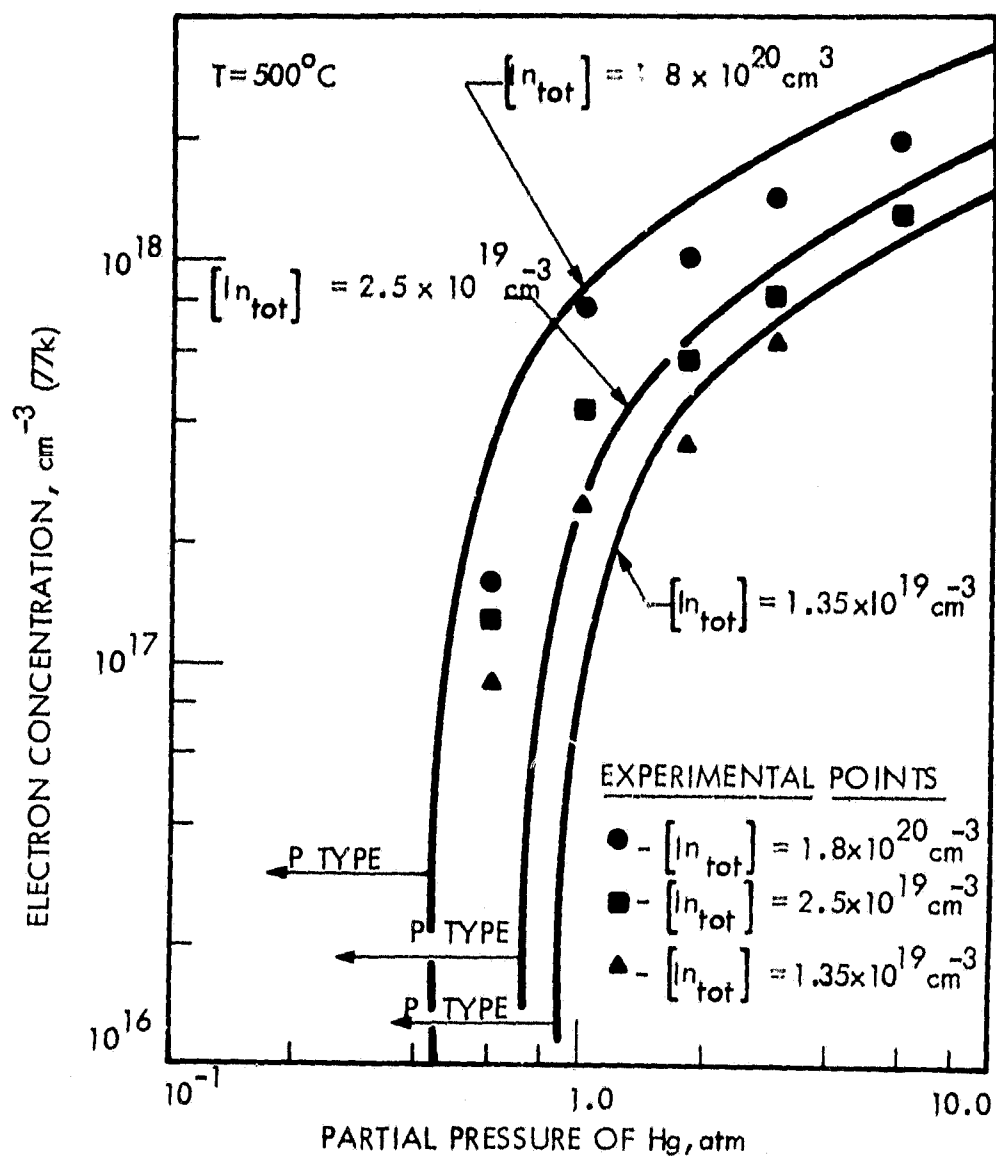


Figure 10: Calculated electron concentration at 77 K in various indium doped Hg_{0.8}Cd_{0.2}Te crystals as a function of the partial pressure of Hg after the crystals are annealed at 500°C and quenched to room temperature; experimental points are also shown for comparison.

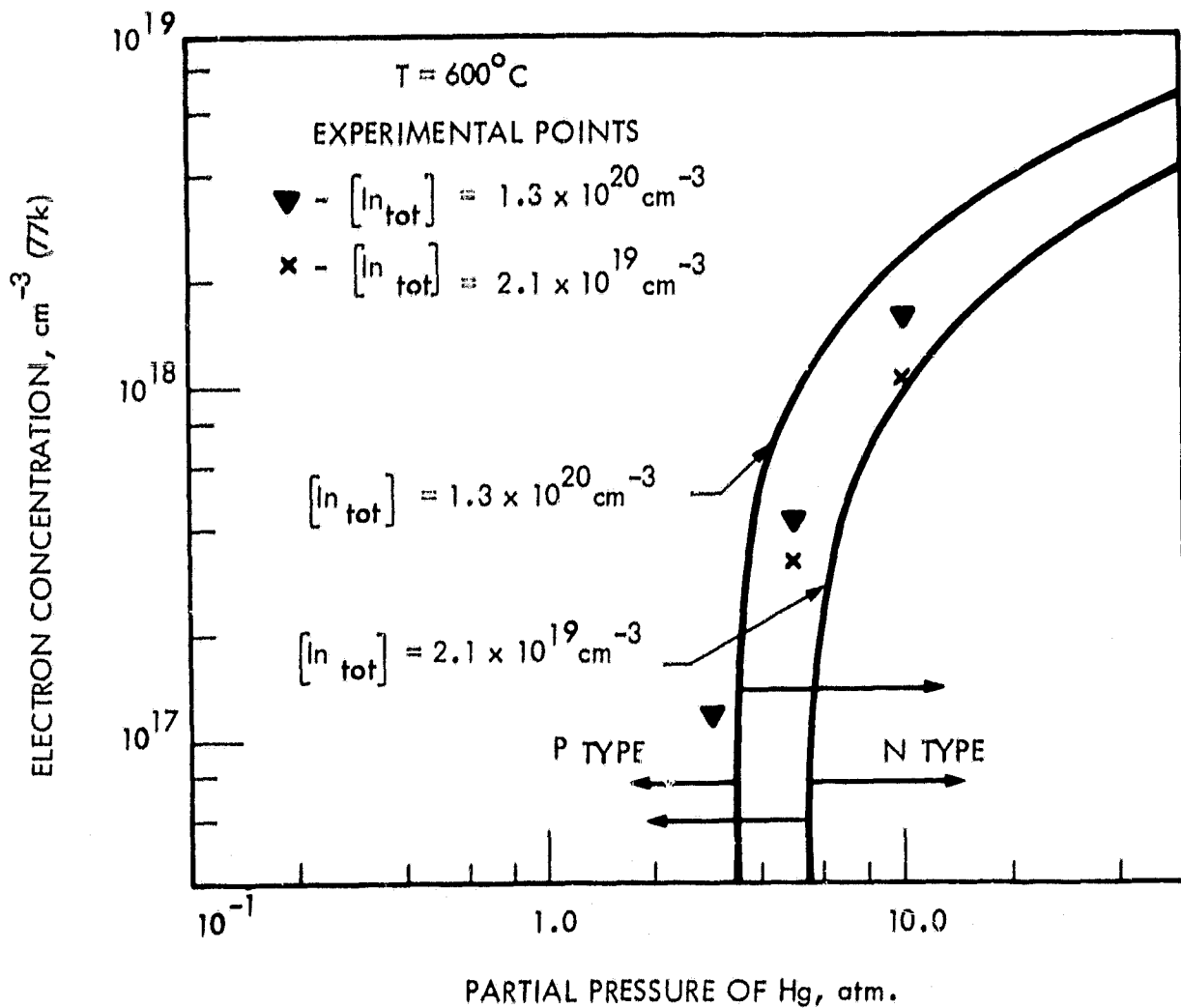


Figure 11: Calculated electron concentration at 77 K in various indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ crystals as a function of the partial pressure of Hg after the crystals are annealed at 600°C and quenched to room temperature; experimental points are also shown for comparison.

EFFECT OF COOLING RATE ON THE ELECTRON CONCENTRATION

The results of Figure 4 indicate that the electron concentration obtained in the indium doped samples which are air cooled from 500°C is higher than in the ones quenched from 500°C, the deviation being greater at lower Hg pressures. This implies that the native acceptor defects frozen in the air cooled samples is lower than in the quenched samples, thereby increasing the electron concentration in the samples air cooled from the equilibration temperatures. It is not presently clear why the native acceptor defects rather than the indium atoms tend to precipitate out during air cooling.

ELECTRON MOBILITY IN THE INDIUM DOPED SAMPLES

As shown in Figure 3, the electron mobility at 77K in the indium doped samples is on the order of 10^4 cm²/vsec, decreasing to lower values for electron concentrations exceeding 10^{18} cm⁻³. These values are an order of magnitude lower than reported previously [7] for low donor concentrations ($<10^{15}$ cm⁻³). The data shown in Figure 3 correspond to various indium doped samples containing indium concentrations varying from approximately 5×10^{18} cm⁻³ to greater than 10^{20} cm⁻³; these samples also contain doubly ionized native acceptor defects varying from 10^{17} cm⁻³ to 5×10^{17} cm⁻³ in concentration corresponding to the annealing temperature of 500-600°C under various partial pressures of Hg. The large electrically active indium concentrations (10^{17} - 10^{18} cm⁻³) and the compensating doubly ionized native defect concentrations probably account for the much lower mobilities.

CONCLUSIONS

A defect model for indium doped Hg_{0.8}Cd_{0.2}Te has been established from Hall effect measurements on indium doped crystals equilibrated under various partial pressures of Hg and temperatures and quenched to room temperature. According to the model, most of the indium is incorporated into the crystals as In₂Te₃(S) dissolved in Hg_{0.8}Cd_{0.2}Te(S) with only a small fraction being present as single donors occupying Hg lattice.

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III.3

**Defect chemistry and characterization of undoped
 $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$**

LATTICE DEFECTS IN $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ALLOYS†

III - DEFECT STRUCTURE OF UNDOPED $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$

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Abstract - Hall effect measurements were carried out on undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ crystals quenched to room temperature subsequent to equilibration at temperatures varying from 450°C to 720°C under various partial pressures of Hg. The variation of the hole concentration as a function of the partial pressure of Hg indicates that the native acceptor defects are doubly ionized. Native donor defects are found to be negligible in concentration and the p-type to n-type conversion is shown to be due to residual donors and not due to native donor defects. Thermodynamic constant for the incorporation of the doubly ionized native acceptor defect has been established.

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*Electrochemical Society active member

Key words - Defect, $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, hole mobility

INTRODUCTION

Schmit and Stelzer [1] have reported electrical data on $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ crystals annealed at various temperatures under Hg saturated and Te saturated conditions. Brebrick and Schwartz [2] have recently analyzed these data on the basis of a defect model that assumes all the p-type crystals to be compensated by native donor defects and predicts the origin of the n-typeness in the crystals to be due to native donor defects. Conclusions of recent defect structure investigation in undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ [3] are in contradiction of those of Brebrick and Schwartz [2]. Since a precise power dependence of the hole concentration on the partial pressure of Hg at the annealing temperatures is not possible to evaluate from the experimental results of Schmit and Stelzer [2], which were done under Hg saturated and Te saturated conditions only, the present work was undertaken to obtain additional electrical data at various intermediate partial pressures of Hg in addition to those of Schmit and Stelzer [1]. These data have enabled us to establish a more precise power dependence of the hole concentration on the partial pressure of Hg at the annealing temperatures; the hole concentration in the cooled crystals has been found to vary as $p_{\text{Hg}}^{-1/3}$ indicating that the dominant native acceptor defects at the annealing temperatures are doubly ionized. Just as for undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ [3] the electrical data in $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ have been explained satisfactorily on the basis that the native acceptor defects are doubly ionized, that the native donor defects are negligible in concentration and that the n-typeness in $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ crystals is due to residual foreign donors. The dependence of the hole concentration on the partial pressure of Hg and the temperature of equilibration has led to the establishment of the thermodynamic constant for the incorporation of the doubly ionized native acceptor defect.

EXPERIMENTAL

The composition of the crystals used in the present work corresponded to $x = 0.4 \pm 0.005$. The residual impurity concentration was $<10^{16} \text{ cm}^{-3}$. In order to improve the efficiency of quenching the high temperature equilibrium, the thickness of the samples was restricted to $<0.004 \text{ cm}$. Equilibration periods ranged from 24 hours at temperatures $>500^\circ\text{C}$ up to 2 to 3 weeks at 450°C .

The procedure of equilibrating the samples in various Hg pressures and quenching the samples subsequent to equilibration is identical to that of Paper I [3]. It should be mentioned here that while Schmit and Stelzer [1] used Te powder along with the samples for equilibration under Te saturated conditions, we have used equivalent Hg pressures [4-6]. Subsequent to the equilibration, the samples were quenched to room temperature. The samples were lapped, polished, and etched in Br-methanol solution. Hall effect and electrical resistivity measurements were made using the van der Pauw method [7]. Magnetic field strengths of 400 Gauss and 4000 Gauss were used for the Hall effect measurements.

RESULTS

• As mentioned in Paper I [3] only those Hall effect results which did not vary with the magnetic field and, thus, showed no mixed type conduction, were used in evaluating the hole concentrations in the samples using the expression:

$$p = \frac{1}{R_H q}$$

Hall coefficient as a function of temperature of measurement is shown in Figure 1 for undoped ($\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$) samples equilibrated at the indicated temperatures and partial pressures of Hg. It can be inferred from the Figure that the ionization of the native acceptor defects appears to be complete around 190-200 K and at higher temperatures intrinsic carriers begin to become important. We have used hole concentration measurements at 192 K to infer the concentration of native acceptor defects present at the equilibration temperatures. Figures 2 and 3 show the hole concentration at 192 K as a function of the partial pressure of Hg for various equilibration temperatures ranging from 450°C to 720°C. The hole concentration increases with decrease in the partial pressure of Hg but more weakly than was found for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ (paper I) [3]. In undoped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ the hole concentration varied as p_{Hg}^{-1} (paper I), whereas, results of figures 2 and 3 indicate that the hole concentration in undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ varies as $p_{\text{Hg}}^{-1/3}$ and increases with increase in temperature.

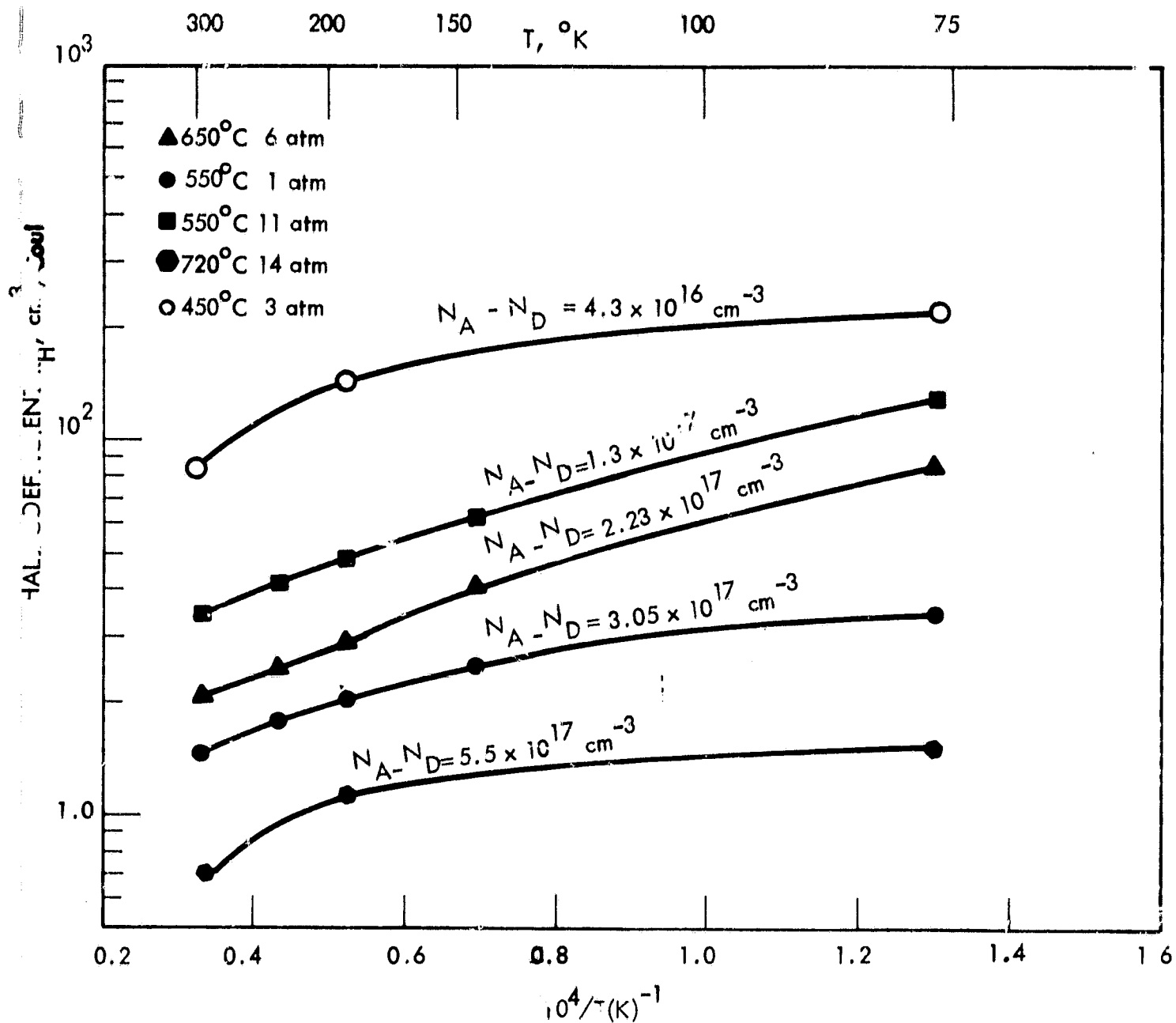


Figure 1. Hall coefficient as a function of measurement temperature for undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ samples annealed at the indicated temperatures and partial pressures of Hg and quenched to room temperature.

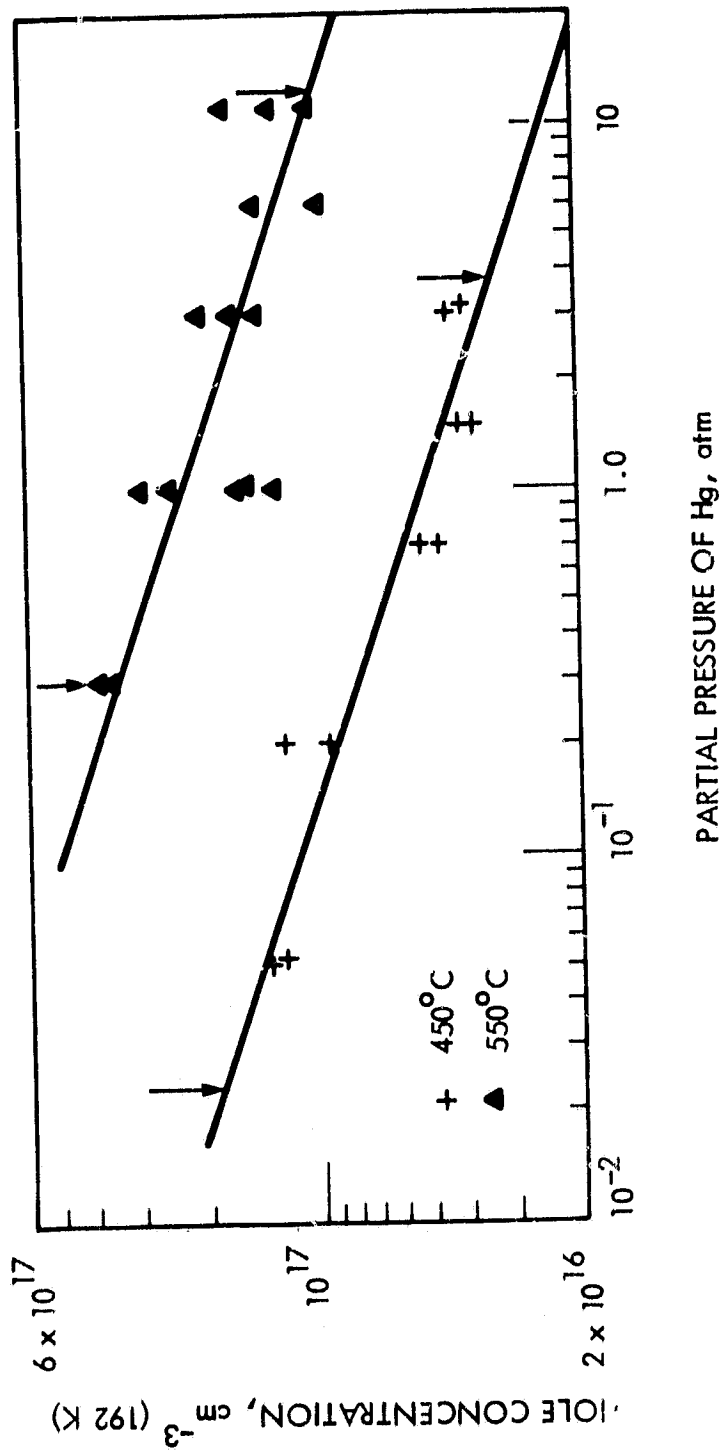


Figure 2. Hole concentration at 192 K as a function of the partial pressure of Hg for undoped Hg_{0.6}Cd_{0.4}Te crystals annealed at 450°C and 550°C and quenched to room temperature; solid lines correspond to the values calculated on the basis of the defect model.

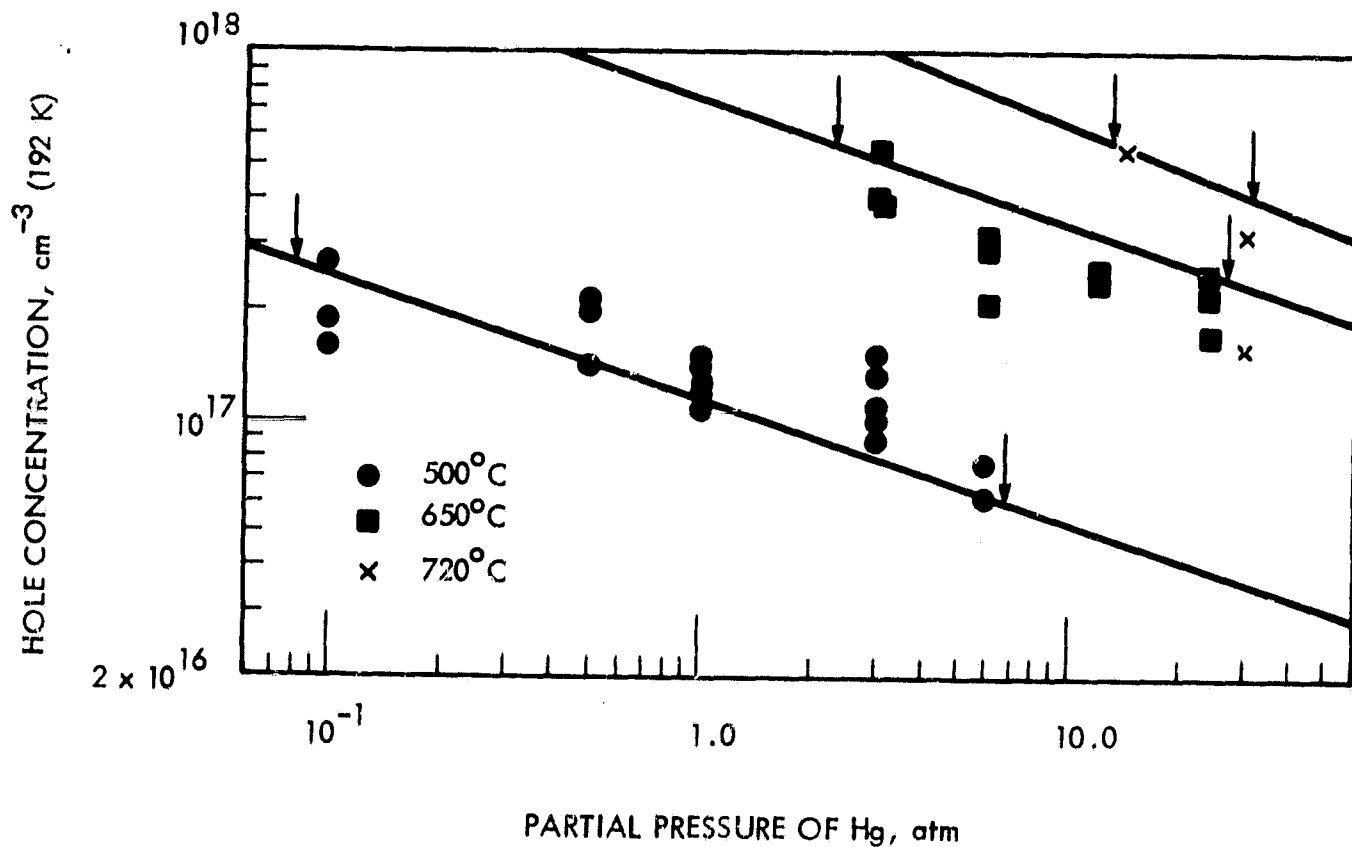


Figure 3. Hole concentration at 192 K as a function of the partial pressure of Hg for undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ crystals annealed at 500°C , 650°C and 720°C and quenched to room temperature; solid lines correspond to the values calculated on the basis of the defect model.

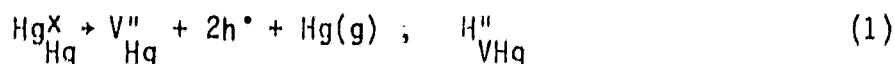
Figures 4 and 5 show the mobility of holes at 77 K and 192 K as a function of the hole concentration. The hole mobilities at 77 K are lower than those obtained for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ (paper I) [3].

DISCUSSION

The quasichemical approach used to arrive at the defect model has already been described in paper I [3] and, hence, will not be detailed here.

NATIVE ACCEPTOR DEFECTS

The fact that the hole concentration in the crystals is proportional to $p_{\text{Hg}}^{-1/3}$ (Figures 2 and 3) indicates that the native acceptor defects are doubly ionized. The formation and ionization of these defects can be described by the following reaction and mass action relation:



$$K_{\text{VHg}}'' = \frac{[\text{V}_{\text{Hg}}'']}{[\text{Hg}_{\text{Hg}}^{\text{X}}]} [\text{h}^{\bullet}]^2 p_{\text{Hg}} \quad (2)$$

If the electroneutrality condition is dominated by V_{Hg}'' and h^{\bullet} then we have

$$[\text{h}^{\bullet}] \approx 2 [\text{V}_{\text{Hg}}''] > [\text{e}']$$

from expression (2) we get:

$$[\text{h}^{\bullet}] = 2 [K_{\text{VHg}}'']^{1/3} p_{\text{Hg}}^{-1/3}$$

The dominance of V_{Hg}'' at the equilibration temperatures implies that the undoped $(\text{Hg}_{0.6}\text{Cd}_{0.4})\text{Te}$ crystals are not intrinsic, unlike undoped $(\text{Hg}_{0.8}\text{Cd}_{0.2})\text{Te}$ crystals [paper I]; in $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$, at the annealing temperatures:

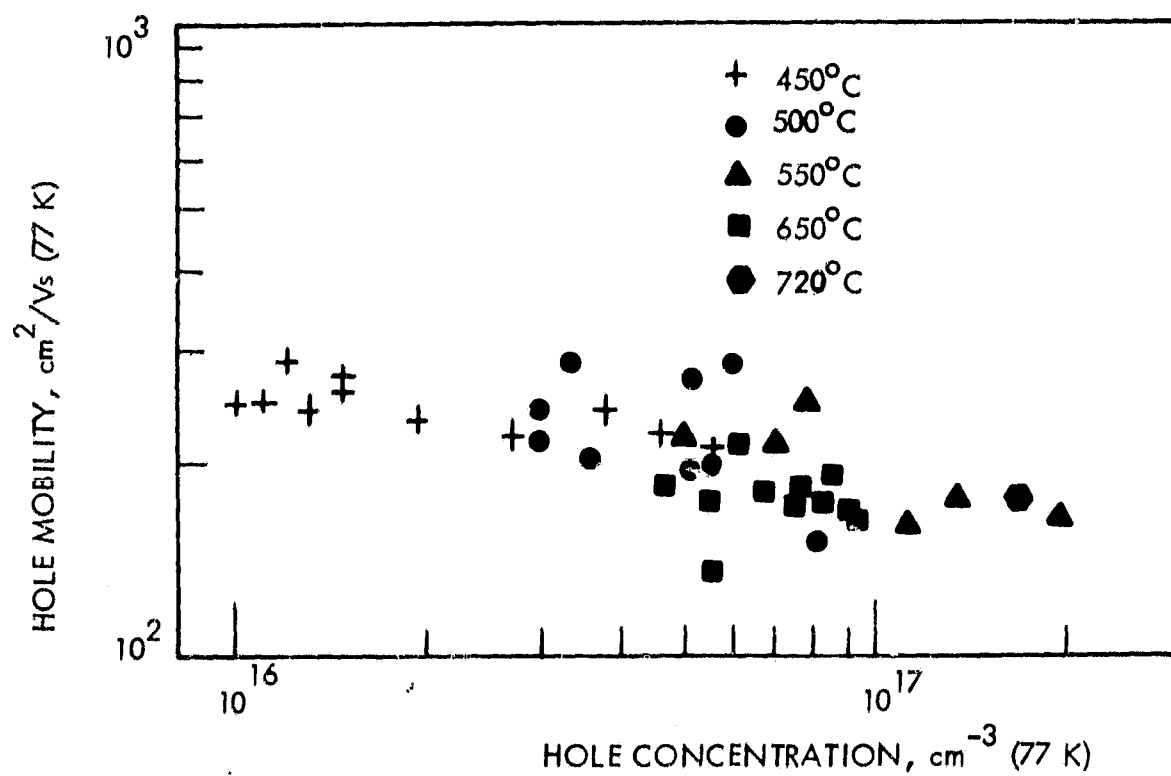


Figure 4. Hole mobility at 77 K as a function of the hole concentration for undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$.

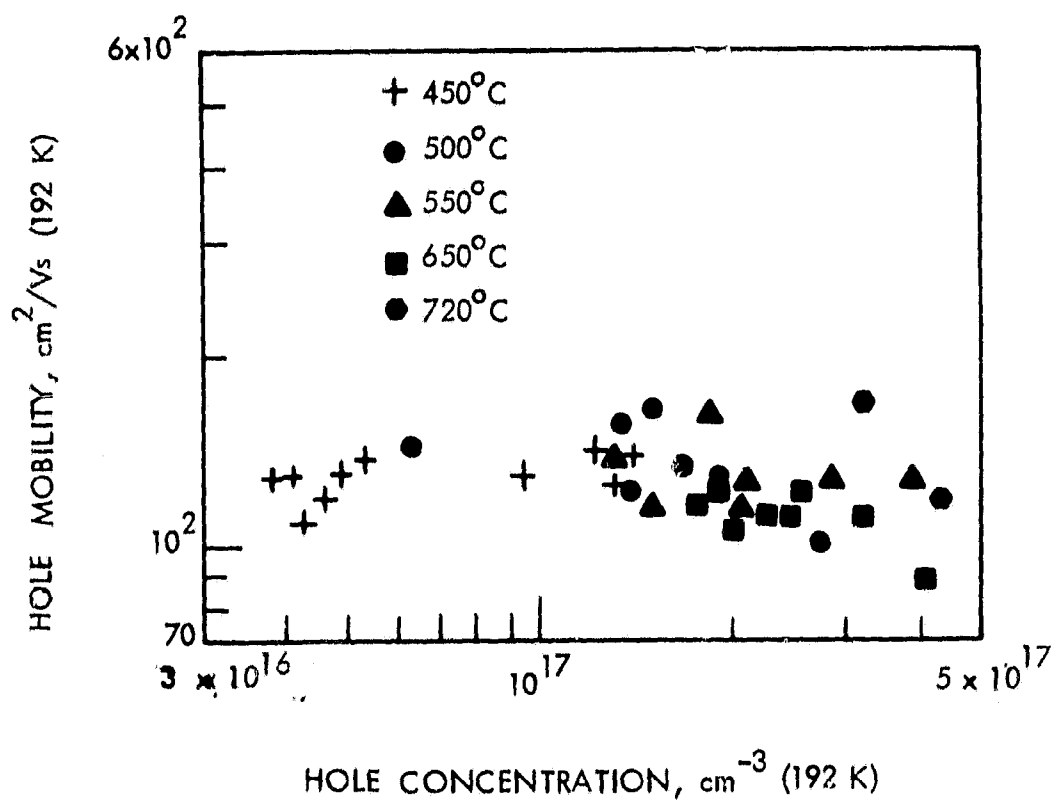


Figure 5. Hole mobility at 192 K as a function of the hole concentration for undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$.

$$[h^{\bullet}] = 2 [V''_{Hg}] > \sqrt{K_i} > [e']$$

whereas, in $Hg_{0.8}Cd_{0.2}Te$:

$$2[V''_{Hg}] < [e'] = [h^{\bullet}] = \sqrt{K_i} \text{ (Paper I).}$$

Thus, although the native acceptor aspects are doubly ionized in both $X = 0.2$ and $X = 0.4$ crystals, the dependence of the hole concentration on the partial pressure of Hg in the cooled crystals is different for the two compositions.

The fact that the intrinsic carrier concentration for the $X = 0.2$ material is higher than that for the $X = 0.4$ is a consequence of the lower bandgap for the $X = 0.2$ material.

COMPARISON OF PRESENT EXPERIMENTAL RESULTS WITH PREVIOUS WORK

Our experimental results differ from those of Schmit and Stelzer [1] at higher temperatures of equilibration as well as for Te saturated conditions. We did not observe any decrease in the hole concentration at $T > 600^{\circ} C$, as found by Schmit and Stelzer. Also, we obtain higher native acceptor defect concentrations (or higher hole concentrations) under Te rich conditions than Schmit and Stelzer did. It is to be noted that the electrical data in reference 1 were obtained for crystals annealed in Hg vapor and Te_2 vapor, with Hg or Te being at the same temperature as $Hg_{0.6}Cd_{0.4}Te$. It is known that the saturation Hg pressure over $Hg_{0.6}Cd_{0.4}Te$ [4-6] is less than that of pure Hg itself, the difference being higher at temperatures greater than $500^{\circ} C$. Hence, by exposing the $Hg_{0.6}Cd_{0.4}Te$ crystals to saturated Hg vapor at greater than $500^{\circ} C$, in the experiments of Schmit and Stelzer [1], compositional changes in the samples may have arisen. Also, similar arguments apply for anneals in saturated Te_2 vapor, reported in reference 1. In addition, it is also known [4-6] that the partial pressures of Te_2 over $Hg_{0.6}Cd_{0.4}Te$ under Te saturated conditions are orders of magnitude lower than partial

pressures of Hg under Te saturated conditions. Hence, depending upon the kinetics of the different equilibration processes and depending upon the fact that during the heat up of the samples and the tellurium source, the sample may not have stayed within the existence region, compositional changes for anneals under Te saturated conditions may also have risen in the experiments of reference 1. In the present work, however, equilibrations under Te saturated conditions were done in Hg vapor at equivalent partial pressures of Hg [4-6] rather than in Te₂ vapor. As discussed in paper I, macroscopic defects such as voids, Hg or Te inclusions, etc., can affect the quenching efficiency of the crystals. Presence of these may also account for the lower hole concentrations obtained by Schmit and Stelzer [1].

P-TYPE TO N-TYPE CONVERSION IN UNDOPED (Hg_{0.6}Cd_{0.4})Te

Schmit and Stelzer [1] found the undoped (Hg_{0.6}Cd_{0.4})Te samples to convert from p-type to n-type under Hg saturated conditions at temperatures below about 350° C. The conversion temperatures for the two crystals that they experimented with were different and the electron concentration in both samples was independent of the equilibration temperature at temperatures below the conversion temperatures. If the p-type to n-type conversion is due to native donor defects, a temperature dependence of the electron concentration should be expected just as is observed for the hole concentration [1] unless the enthalpies associated with the vaporization of Hg(l), the intrinsic excitation constant and the incorporation of the native donor defects are of such a sign and magnitude that the electron concentration in the cooled crystals is independent of the anneal temperature. For details see Appendix of paper I. However, if the conversion is due to native donor defects the p-type to n-type conversion temperature should be the same for different samples as long as native donor defects are larger in concentration than the foreign donors. Thus, even if the temperature independence of electron concentration under Hg saturated conditions can be explained on the basis of native donor defects, different conversion temperatures for different samples cannot be explained unless the conversion is due to foreign donor impurities present in the crystals. Hence, the concentration of native donor defects in undoped (Hg_{0.6}Cd_{0.4})Te crystals appears to be negligible and, at least, less than 10^{15} cm⁻³ at 300° C.

ABSENCE OF COMPENSATION

While attempting to explain the low experimental mobilities of holes in $(\text{Hg}_{0.6}\text{Cd}_{0.4})\text{Te}$, Scott et al [8] assumed that all the undoped p-type samples were heavily compensated. This implied that the compensation mechanism in their crystals was probably a result of the dominance of either Schotky defects $([\text{V}^{\bullet\bullet}\text{Hg}] = [\text{V}_{\text{Te}}^{\bullet\bullet}])$ or Frenkel defects $([\text{V}^{\bullet\bullet}\text{Hg}] = [\text{Hg}_i^{\bullet\bullet}])$ [2]. Evidence of any such compensation in our samples is lacking. Figure 4 indicates that the hole mobilities at 77 K vary (although only weakly) as a function of only the hole concentration in the crystals, irrespective of the partial pressure of Hg and temperature of anneal. If there was any compensation by native donor defects the concentration of these defects can be expected to be exponentially dependent on temperature and the mobility-dependence on the hole concentration would not have been as linear as shown in Figure 4.

It should be pointed out that mobility results similar to those of Scott et al [8] mentioned above, have been observed by others [9-14]. For instance, electron and hole mobilities less than predicted by the Brooks-Herring expression for the ionized impurity scattering [9] have been reported by Reynolds et al [10] for $(\text{Hg}_{0.8}\text{Cd}_{0.2})\text{Te}$. These authors explain the discrepancy to be due to the inadequacy of the Brooks-Herring formula for doping levels on the order of 10^{16} cm^{-3} in the n-type material and of 10^{18} cm^{-3} in the p-type material and they chose not to invoke compensation as the reason. Ionized impurity mobility calculations at 77 K in degenerately doped n-type GaAs [11], n-type HgSe [12] and p-type Ge [13] at 77 K where the Brooks-Herring formula has considerably overestimated the mobilities due to ionized impurity scattering have also been reported. Recent calculations of Nishizawa, et. al., [14] for hole mobilities due to ionized impurity scattering in $(\text{Hg}_{0.82}\text{Cd}_{0.18})\text{Te}$ yielded values 4.5 times larger than the experimentally measured mobilities. According to these authors, the discrepancy between the theoretical and experimental mobilities of holes due to ionized impurity scattering is a common feature of many semiconductors. In view of these arguments it appears that more thorough calculations of hole mobilities in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys is needed.

MASS ACTION CONSTANT K''_{VHg}

Since the power dependence of the hole concentration on the partial pressure of Hg in the cooled crystals does not appear to be greater than 1/3, the only dominant species at the annealing temperatures appear to be the holes and the native acceptor defects ($[e'] \ll [V''_{Hg}] = [h^*]/2$). Assuming that $[h^*] = 2 [V''_{Hg}]$ at the high temperature as well as in the cooled crystals, from equation 2 we get:

$$K''_{VHg} = [h^*]^3/2 p_{Hg} \quad (3)$$

Using a procedure of trial and error, an expression for K''_{VHg} in the form of $Ae^{-Q/kT}$ was arrived at, which best explained the experimental results of Figures 2 and 3 at various temperatures. Greater emphasis was placed on the results at lower annealing temperatures with the assumption that results from the highest temperature anneals may suffer from a greater quenching inefficiency. The value of K''_{VHg} was evaluated to be:

$$K''_{VHg} = 6.61 \times 10^{65} \exp(-2.29 \text{ eV}/kT) (\text{cm}^{-9} \text{ atm}) \quad (4)$$

or, in terms of site fractions, (there are 1.48×10^{22} molecules/cm³ in $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$)

$$K''_{VHg} = 0.204 \exp(-2.29 \text{ eV}/kT) \text{ site fr}^3 \text{ atm} \quad (5)$$

The hole concentrations calculated based on this value of K''_{VHg} are shown in Figures 2 and 3 as solid lines. The agreement between the experimental results and the calculated values appears satisfactory.

Since $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ melts at a higher temperature than $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ and has a greater band gap, the enthalpy associated with the incorporation of the doubly ionized acceptor defect can be expected to be higher in $X = 0.4$ material than in $X = 0.2$ material. The enthalpy for $x = 0.4$ from equation 4 is 2.29 eV, whereas, that for $X = 0.2$ material established in paper I is 2.24 eV.

Since the intrinsic carriers do not dominate the electroneutrality condition in $X = 0.4$ material for temperatures between $450 - 720^\circ \text{C}$, evaluation of the intrinsic excitation constant $K_i = [e'] [h^*]$ was not possible. However, from the results of figures 2 and 3 it appears that the intrinsic carrier concentration is less than $3 \times 10^{16} \text{ cm}^{-3}$ at 450°C and less than $3 \times 10^{17} \text{ cm}^{-3}$ at 720°C . These upper limits of the intrinsic carrier concentrations are lower than those extrapolated from the empirical expressions for n_i for $X = 0.4$ in literature [15].

HOLE CONCENTRATIONS FOR ANNEALS UNDER Hg SATURATED AND Te SATURATED CONDITIONS

With the knowledge of the partial pressures of Hg under Hg saturated and Te saturated conditions [4-6] and the value of $K''_{V_{\text{Hg}}}$ (expressions 4 and 5) established in the previous section, the hole concentrations in the crystals cooled to room temperature after anneals at different temperatures can be calculated from equation 3. Figure 6 shows the calculated hole concentrations under Hg saturated and Te saturated conditions. It is to be noted that the calculations assume the concentrations of the residual donors and acceptors to be negligible in comparison with the native defect concentrations at the anneal temperatures. Figure 6 shows the experimental results of the present work, as well as, those of Schmit and Stelzer [1]. It is clear from the figure that quenching inefficiencies or the presence of voids and inclusions in the material [Paper I] can cause scatter in the data, particularly at higher temperatures. Also, the decrease of hole concentration with increase in temperature at $T > 600^\circ \text{C}$ for Hg saturated conditions observed in reference 1 appears to arise from the quenching inefficiencies and is not a real effect since our results show a continuous increase in hole concentration with increase of temperature from $450 - 720^\circ \text{C}$. Residual impurity concentrations were neglected in the electroneutrality condition used to arrive at the hole concentration calculations detailed in the previous section. At lower temperatures of annealing the presence of residual donor concentrations can considerably affect the hole concentration in the samples. Appendix 1 details the calculation of the hole concentration in the crystals in the presence of residual donors.

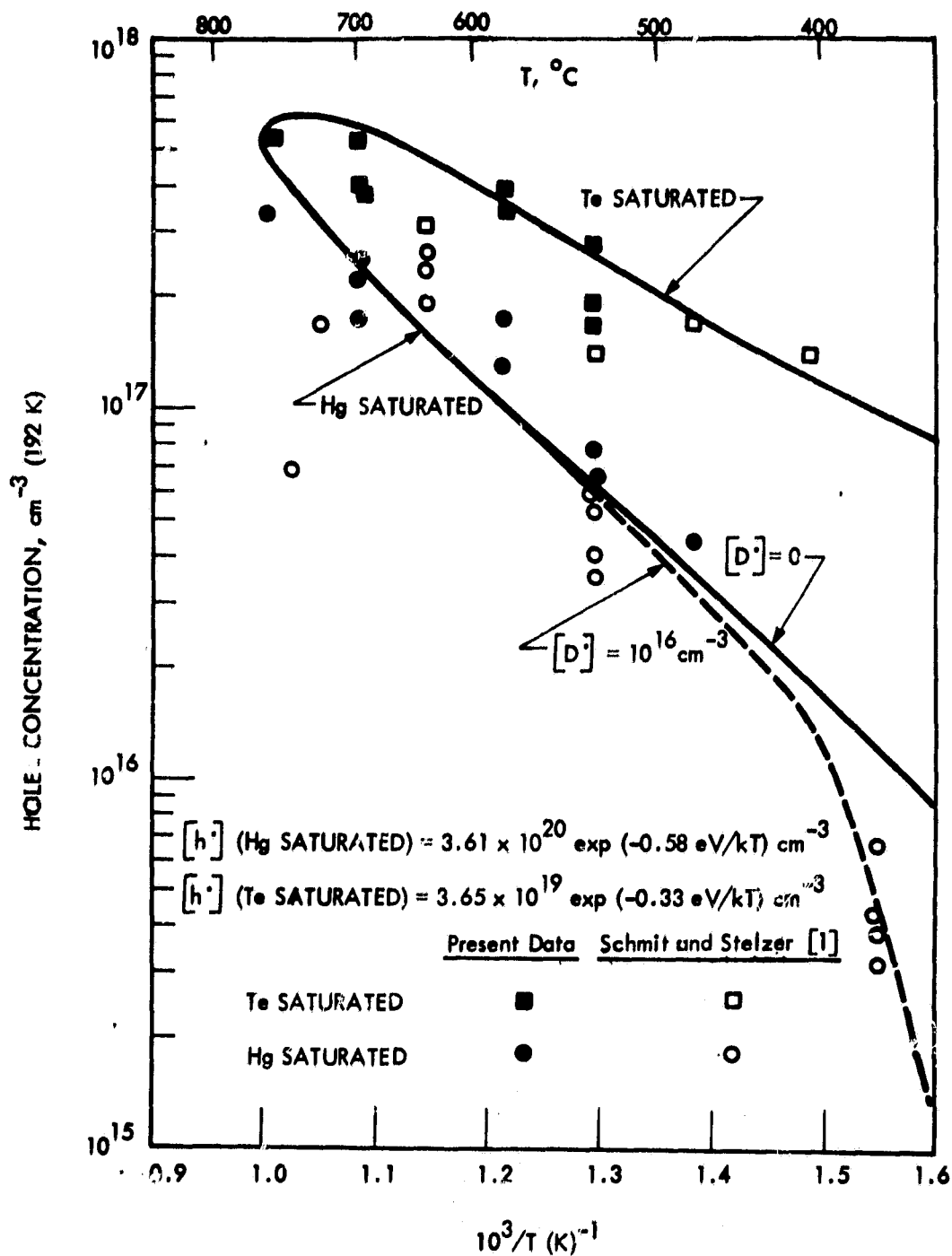


Figure 6. Calculated hole concentration lines at 192 K as a function of annealing temperature for undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ equilibrated in Hg and Te saturated conditions.

Such a calculation assuming a residual donor concentration of 10^{16} cm^{-3} , is shown as a dashed line in Figure 6. It is clear from the figure that the results of reference 1 at 375°C under Hg saturated conditions can be explained if the crystals are assumed to have approximately 10^{16} cm^{-3} residual donors.

The expressions for the hole concentrations in the cooled crystals as a function of temperature for Hg saturated and Te saturated conditions are given by:

$$[h'] \text{ (Hg saturated)} = 3.61 \times 10^{20} \exp (-0.58 \text{ eV/kT}) \text{ cm}^{-3} \quad (6)$$

and

$$[h'] \text{ (Te saturated)} = 3.65 \times 10^{19} \exp (-0.33 \text{ eV/kT}) \text{ cm}^{-3} \quad (7)$$

ISO HOLE CONCENTRATION PLOT

Hole concentration calculations as a function of the anneal temperature and the partial pressure of Hg as detailed in the two previous sections enable us to draw lines of constant deviation from stoichiometry as a function of temperature and partial pressure of Hg. A plot of such lines of constant hole concentration is shown in Figure 7. The upper and lower Hg pressures within which the solid is stable at each temperature were obtained from references [4-6]. Comparison of this plot with a similar one for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ (Paper I, Figure 16) indicates that the concentration of native acceptor defects obtained in $x = 0.4$ material is lower than in $x = 0.2$ material. The temperature dependence of the hole concentration in the cooled crystals is also shallower for $x = 0.4$ than for $x = 0.2$ owing to the fact that the $x = 0.2$ crystals are intrinsic at the anneal temperatures, whereas, $x = 0.4$ crystals are not.

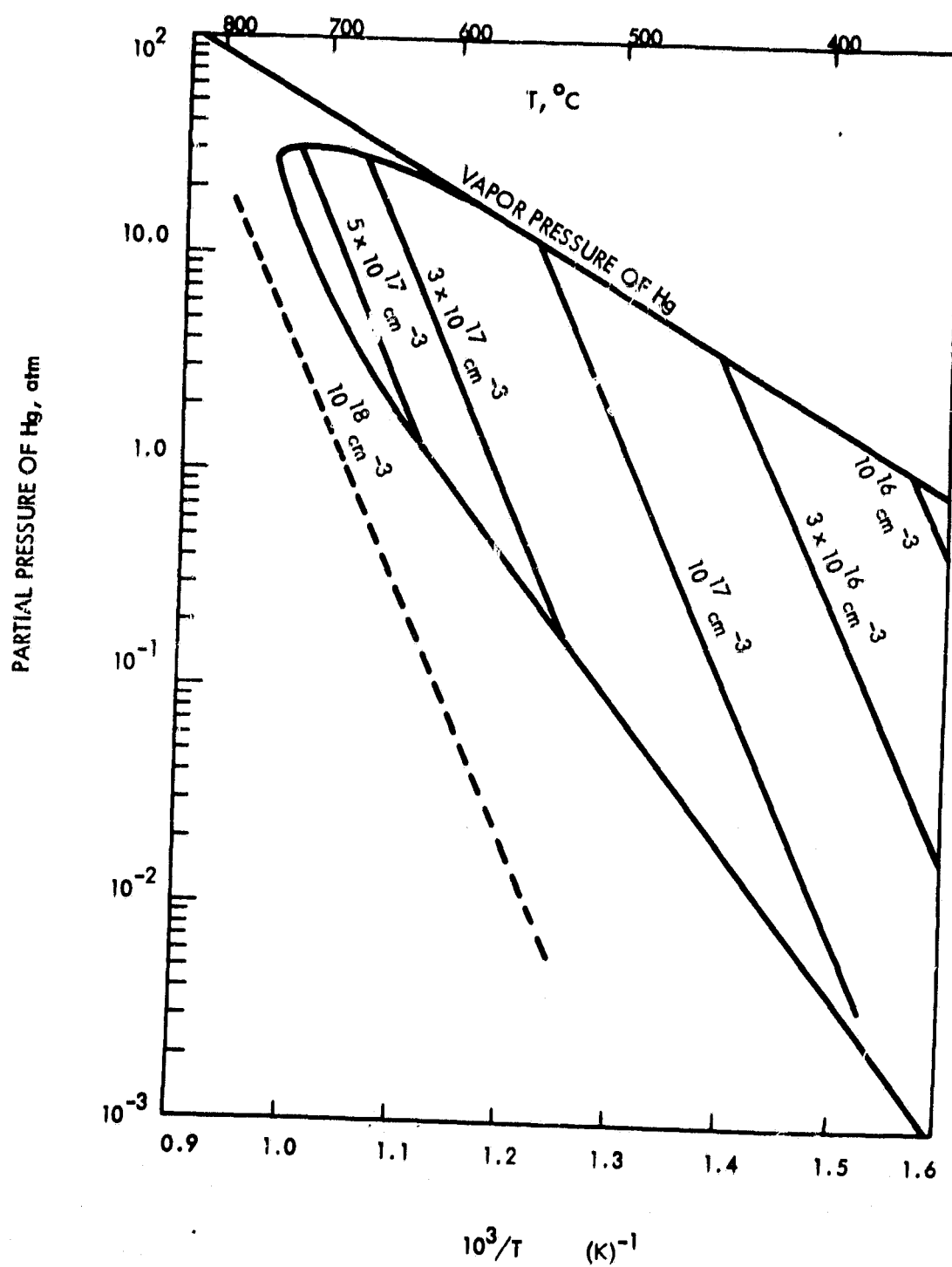


Figure 7. Calculated ISO hole concentration lines at 192 K for $Hg_{0.6}Cd_{0.4}Te$ as a function of the partial pressure of Hg and temperature of annealing.

HOLE MOBILITY IN $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$

Figures 4 and 5 show that the hole mobility at 77 K decreases with increase in hole concentration whereas it is relatively independent of the hole concentration at 192 K indicating that the hole mobility at 192 K is almost completely dominated by lattice scattering whereas ionized impurity scattering contributes to the mobility at 77 K. The absolute hole mobility at 77 K as well as its dependence on the hole concentration in $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ are less than in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ (paper I) [3]; the larger band gap of $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ and hence a probably larger effective mass of holes accounts for a larger contribution from lattice scattering to the hole mobility at a given temperature.

CONCLUSION

Based on the variation of the hole concentration as a function of the partial pressure of Hg in crystals annealed at various temperatures and quenched to room temperature, the dominant native acceptor defects in undoped $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ have been established to be doubly ionized. The mass action constant describing the incorporation of the doubly ionized acceptor defect explains the experimental results satisfactorily.

ACKNOWLEDGEMENT

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APPENDIX 1

HOLE CONCENTRATION CALCULATIONS IN $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$ CONTAINING RESIDUAL DONORS

Electroneutrality Condition:

High temperature

$$2[V''_{\text{Hg}}]_{\text{HT}} = [h^{\bullet}]_{\text{HT}} + [D^{\bullet}] \quad (1)$$

Cooled crystals

$$[h^{\bullet}]_{\text{LT}} = 2 [V''_{\text{Hg}}]_{\text{HT}} - [D^{\bullet}] \quad (2)$$

Subscripts HT and LT in equations 1 and 2 refer to the high temperature and low temperature defect states respectively; $[D^{\bullet}]$ refers to concentration of residual donors in the samples, assumed to be always ionized and independent of anneal temperature.

Expressing the species in equations (1) and (2) in terms of the mass action constant K''_{VHg} (equation 2 of main text) we get,

$$2 K''_{\text{VHg}} / [h^{\bullet}]_{\text{HT}}^2 p_{\text{Hg}} = [h^{\bullet}]_{\text{HT}} + [D^{\bullet}]$$

or
$$[h^{\bullet}]_{\text{HT}}^3 + [h^{\bullet}]_{\text{HT}}^2 [D^{\bullet}] = 2 K''_{\text{VHg}} / p_{\text{Hg}} \quad (3)$$

In the cooled crystals,

$$[h^{\bullet}]_{\text{LT}} = 2 K''_{\text{VHg}} / [h^{\bullet}]_{\text{HT}}^2 p_{\text{Hg}} - [D^{\bullet}] \quad (4)$$

with the knowledge of K''_{VHg} (equation 2 of the main text) hole concentration in the cooled crystals can be calculated from equations 3 and 4 for various fixed residual donor concentrations in the crystals.

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IV. PLANS FOR FURTHER WORK

With the knowledge of the defect situation in undoped, copper doped and indium doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ it should now become possible to investigate the behavior of dopants which are more complex in behavior. Phosphorus appears to be such a dopant and investigation of the defect structure of phosphorus doped $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ has just begun; $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ crystals doped with two different phosphorus concentrations have been grown and the electrical properties are being evaluated. Halogen impurities are a frequent source of donor contamination in II-VI compounds and hence behavior of Iodine as a halogen donor in $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te(S)}$ is also being investigated.